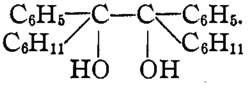
son.[13] When this ketone was treated with magnesium and iodine according to the method of Gomberg and Bachmann,[14] it was recovered unchanged. Magnesium amalgam in benzene followed by water did not cause reduction. Sodium and alcohol reduced the ketone to give a 76% yield of dicyclohexyl carbinol.

## Summary

1. Cyclohexylmagnesium bromide reacts with esters of oxalic acid to give as the main product the corresponding ester of dicyclohexylglycolic acid. Small amounts of tetracyclohexyl ethylene glycol can be obtained.

2. Ethyl dicyclohexylglycolate does not react readily with either ethylmagnesium bromide, phenylmagnesium bromide or cyclohexylmagnesium bromide.

3. Methyl benzilate reacts with cyclohexylmagnesium bromide to give an hydroxy ketone, $(C_6H_5)_2C(OH)COC_6H_{11}$.

4. Benzil reacts with cyclohexylmagnesium bromide to give the symmetrical diphenyl dicyclohexyl ethylene glycol,  $C_6H_5(C_6H_{11})C(OH){-}C(OH)(C_6H_{11})C_6H_5$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ST. STEPHEN'S COLLEGE]

# ORGANIC SELENIUM COMPOUNDS. SOME DERIVATIVES OF AROMATIC SELENO-ETHERS

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## Introductory

The researches reported in this paper originated in an attempt to duplicate, with compounds containing selenium, certain investigations conducted by Reid, with the senior author of this paper,[1] and with other investigators,[2,3] upon the influence of a sulfur atom in varying positions in the molecule on the color of a series of azo dyes. It had been our intention to employ exactly analogous methods to those outlined in references (1) and (2) in order to prepare nitro seleno-ethers, $O_2NC_6H_4SeR$, and from them amino seleno-ethers of the type, $H_2NC_6H_4SeR$, which could be diazotized and coupled with standard intermediates to give azo dyes.

These methods were found to be completely unfruitful because of the instability of the *o*- and *p*-nitroselenophenols, $O_2NC_6H_4SeH$, which oxidize

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[13] Private communication.

[14] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

[1] Foster and Reid, THIS JOURNAL, **46**, 1936 (1924).

[2] Waldron and Reid, *ibid.*, **45**, 2399 (1923).

[3] Palmer and Reid, *ibid.*, **48**, 528 (1926).

rapidly back to the diphenyl diselenides, $O_2NC_6H_4Se_2C_6H_4NO_2$, on coming in contact with the air like their sulfur analogs.[4,5]

We then tried to nitrate some seleno-ethers, $C_6H_5SeR$, with a nitrating mixture, by Gattermann's method, without results. Fuming nitric acid, however, did react with phenyl seleno-ethers, giving some crystallizable solids, but the reaction was found to be oxidation rather than nitration and no nitro group could be detected in the products. The oxidation products produced by this method seemed to be sufficiently interesting and sufficiently different from their sulfur analogs to warrant a special investigation, the results of which are set down in this paper.

## Theoretical and Experimental

The most interesting differences between the aromatic seleno-ethers and the corresponding sulfur compounds are the increasingly basic properties of oxidized selenium, shown by the tendency to form loose molecular addition products, and the tendency of the former substances to exist in the hexavalent rather than in the tetravalent condition. Stoecker and Krafft[6] have reported the formation of a hydronitrate of benzene seleninic acid, $C_6H_5SeO_2H\cdot HNO_3$; Jackson[7] has reported the same phenomenon with benzyl seleninic acid, $C_6H_5CH_2SeO_2H$, and Shaw and Reid[8] with methyl seleninic acid, $CH_3SeO_2H$, and with ethyl seleninic acid, $C_2H_5SeO_2H$. So far as we can discover, however, there is no record of the production of hydronitrates of the selenoxides, $C_6H_5SeOR$. We have studied the formation of a number of these selenoxides by a variety of methods, have prepared the hydronitrates of some of them and have evolved a theory for the mechanism of the rather unusual action of the halogen acids upon them.

By the treatment of the sodium salt of selenophenol, $C_6H_5SeNa$, with alkyl halides, we have prepared the following seleno-ethers: (1), $C_6H_5SeCH_3$;[9] (2), $C_6H_5SeC_2H_5$; (3), $C_6H_5SeC_5H_{11}$ (*iso*); (4), $C_6H_5SeC_6H_5$.[9]

The last compound was also procured as a by-product in the preparation of selenophenol by redistillation of the high-boiling fraction. We have treated all of these substances with a number of oxidizing agents: with fuming nitric acid, with chromic acid, with potassium permanganate and with hydrogen peroxide. Hydrogen peroxide has no effect, due probably to the small solubility of the substances in water. Chromic acid in acetic acid solution produces tarry mixtures impossible to purify. Nitric acid and potassium permanganate, however, give substances that

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[4] Lecher and Simon, *Ber.*, **55**, 2426 (1922).

[5] Brand and Wirsing, *Ber.*, **46**, 822 (1913).

[6] Stoecker and Krafft, *Ber.*, **39**, 2200 (1906).

[7] Jackson, *Ann.*, **179**, 13 (1875).

[8] Shaw and Reid, THIS JOURNAL, **48**, 520 (1926).

[9] Prepared by other workers.

can be separated either as the hydronitrates or as chlorine addition products. These latter are not derivatives of selenoxides.

## Preparation of Materials

**Preparation of Selenophenol,** $C_6H_5SeH$.—This compound was prepared by the Grignard reaction according to the method of Taboury[10] with the following modifications. After treating phenylmagnesium bromide with selenium and decomposing the intermediate formed with cold hydrochloric acid, we separated the ether layer, extracted the solution with more ether and combined the ether extracts. These we shook up with one equivalent of sodium hydroxide, calculated on the basis of the total amount of selenium used, and dissolved in water to make a 25% solution. The ethereal extracts were then dried with calcium chloride, the ether was evaporated and from the residue were recovered by distillation diphenyl diselenide and considerable quantities of diphenyl monoselenide, boiling at 303°. The sodium hydroxide solution was then acidified with a slight excess of concentrated hydrochloric acid, cooled and extracted three times with ether. The residue recovered from the ether consisted of almost pure selenophenol, b. p. 182°, which was further purified by distillation.

**Preparation of the Seleno-Ethers,** $C_6H_5SeR$.—The methyl derivative, $C_6H_5SeCH_3$, was prepared by the method of Pope and Neville;[11] the others by dissolving selenophenol in one equivalent of sodium hydroxide in the minimum quantity of water, adding 50 cc. of absolute alcohol and then the alkyl halide. The mixture was refluxed for fifteen minutes, diluted with four times its volume of cold water, extracted three times with ether, the ether separated, washed with water, dried over calcium chloride and distilled off. The remaining oils were rectified. Methyl iodide was used for the methyl derivative and the bromides of the other alkyls. The experiments are summarized in Table I.

TABLE I

PREPARATION OF THE SELENO-ETHERS

| $C_6H_5SeR$, R | Seleno-phenol, g. | Halide, g. | Yield, g. | Yield, % | B. p., °C. | Analysis for Se, Calcd. | Analysis for Se, Found |
|---|---|---|---|---|---|---|---|
| $C_2H_5$ | 10 | 20 | 8.5 | 72 | 214–216 | 42.44 | 42.35 |
| $C_5H_{11}$, *iso* | 18 | 20 | 22.5 | 86.5 | 105° (3 mm.) | 34.84 | 34.24 |
| $C_6H_5$[a] | 10 | 10 | 3.5 | 24 | 303° | ... | ... |

[a] Butyl alcohol was used as a solvent with the phenyl derivative.

**Diphenyl Selenium Oxide,** $(C_6H_5)_2SeO$.—This substance was used in checking, by analogy, the constitution of our products. We prepared it from diphenyl selenium dichloride, $(C_6H_5)_2SeCl_2$, and sodium hydroxide by Krafft and Vorster's method[12] and also from diphenyl selenoxide hydronitrate. 1.75 g. of $(C_6H_5)_2SeO:HNO_3$ was treated with sodium carbonate and extracted with alcohol according to the procedure outlined on p. 1185 and summarized in Table III. A white, granular solid was obtained which was recrystallized from dry benzene; yield of crude product, theoretical; m. p. 106–108°.

*Anal.* Calcd. for $C_{12}H_{10}SeO$: Se, 31.73. Found: Se, 31.86.

Analyses for chlorine were accomplished by dissolving weighed samples in water and precipitating silver chloride from the slightly acidified solution with 0.1 *N* silver nitrate solution. Selenium analyses were made by

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[10] Taboury, *Ann. chim. phys.*, **15**, 5 (1908).

[11] Pope and Neville, *J. Chem. Soc.*, **81**, 1553 (1902).

[12] Krafft and Vorster, *Ber.*, **26**, 2818 (1893).

Shaw and Reid's method,[13] the improved directions for which have been published since the completion of our work.[14]

**The Action of Nitric Acid on the Seleno-Ethers.**—Methylphenyl, ethylphenyl and *iso*-amylphenyl selenides react with fuming nitric acid violently in the cold, with evolution of much heat and oxides of nitrogen. The reaction mixtures were heated on the steam-bath until no more $NO_2$ was evolved. The methyl derivative only, however, gives a crystalline solid, which comes out of the reaction mixture in white plates or needles, on evaporation and cooling, consists of the hydronitrate of methylphenyl selenium oxide, $C_6H_5SeOCH_3 \cdot HNO_3$ and melts at 97°. The other two compounds gave water soluble oils which are insoluble in organic solvents and decompose too easily to be purified by distillation (ethylphenyl selenoxide hydronitrate decomposes at 110° under 3 mm. pressure). Consequently their constitution can only be assumed by analogy to the methyl and phenyl derivatives. If heated much above 100°, all three compounds decompose, with evolution of $NO_2$, leaving behind diphenyl diselenide, melting at 63°, which we identified by a mixed melting point with a sample of diphenyl diselenide obtained as a by-product in the preparation of selenophenol. An attempt to identify the other products of the decomposition, made with the methyl derivative, was unsuccessful, so that we cannot at present write an equation for this reaction. The details of these processes will be found in Table II.

TABLE II

PREPARATION OF THE SELENOXIDE HYDRONITRATES

$C_6H_5SeOR \cdot HNO_3$

| R | Seleno-ether, g. | $HNO_3$, cc. | Yield, g. | % | M. p., °C. | Analysis for Se Calcd. | Found | Physical form and color |
|---|---|---|---|---|---|---|---|---|
| $CH_3$ | 15 | 16 | 21 | 64 | 97 | 31.38 | 31.24–31.21 | White needles or plates |
| $C_2H_5$ | 15 | 20 | .. | .. | .. | ... | ... | Colorless oil |
| $C_5H_{11}$ | 30 | 40 | .. | .. | .. | ... | ... | Colorless oil |
| $C_6H_5$ | 15 | 20 | 15.5 | 77 | 97 | 25.16 | 25.47–25.47 | White needles |

The oils obtained were treated directly by the process of Table III.

When these hydronitrates are treated in water solution with sodium carbonate one mole of the carbonate is taken up, carbon dioxide is evolved and evaporation to dryness and extraction with alcohol or benzene yields oils which are undoubtedly the selenoxides, $C_6H_5SeOR$, but which again are too little soluble and decompose too easily to be purified. When these oils are treated with concentrated hydrochloric acid (the

TABLE III

PREPARATION OF THE DICHLORIDES, $C_6H_5SeCl_2R$, BY THE ACTION OF $Na_2CO_3$ AND HCL ON THE HYDRONITRATES OR OXIDES

| R | Starting compound, g. | Yield g. | % | Mixed m. p., °C. |
|---|---|---|---|---|
| $CH_3$ | $C_6H_5SeOR:HNO_3$ 20 | 10 | 97 | 122 (dec.) |
| $C_2H_5$ | (Unpurified oil from Table II) | | | 64–65 |
| $C_5H_{11}$ | (Unpurified oil from Table II) | | | (Gave benzene seleninic acid, $C_6H_5SeO_2H$, mixed m. p., 121–122°) |
| $C_6H_5$ | $C_6H_5SeOR:HNO_3$ 2 | 1 | 77 | 142 (dec.)[a] |
| $C_6H_5$ | $(C_6H_5)_2SeO$ 2 | 1.4 | 57 | 142 (dec.)[a] |

[a] Krafft and Vorster report a melting point of 178° (dec.) for this substance.

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[13] Private communication of Edwin H. Shaw.

[14] Shaw and Reid, THIS JOURNAL, 49, 2330 (1927).

*iso*-amyl derivative could be dissolved in benzene and saturated with hydrogen chloride gas) they are converted to white solids, crystallizable from benzene, xylene, alcohol or dry ether, which, except the *iso*-amyl derivative, analyze for the dichlorides, $C_6H_5$-$SeCl_2R$. The methyl derivative was readily reconverted to the hydronitrate by dissolving it in concentrated nitric acid, a reaction which is typical of the selenoxides.[12] Impure ethylphenyl selenium dichloride decomposed rapidly on standing in a desiccator and this method of preparing it was consequently abandoned in favor of the better one described below. All of these procedures are summarized in Table III, which includes for convenience the phenyl derivative described below.

The compounds were identified by taking mixed melting points with samples prepared by the method outlined in Table IV.

Because of our inability to obtain isolable intermediates, the reactions described above were not entirely satisfactory. In order to check them we decided to carry them out upon the phenyl analog of the compounds we had used, namely, diphenyl diselenide, $(C_6H_5)_2Se$, which gave promise of better results. In fact, diphenyl selenium oxide had already been described by Krafft and Vorster,[12] but it had never been prepared by oxidation with nitric acid and its hydronitrate was unknown. In our first attempt we oxidized the high-boiling fraction (295–305°) of the by-products obtained in making selenophenol by the Grignard reaction, which should have consisted chiefly of diphenyl selenide.[10] It gave, however, a mixture of three solids, melting at 95–98°, 130–135°, and 226–228°, respectively, which we did not attempt to identify. We then prepared pure diphenyl selenide from sodium selenophenolate and bromobenzene (see Table I) and from this were able to procure a hydronitrate, $(C_6H_5)_2SeO{\cdot}HNO_3$, which melted at 97° (see Table II). Sodium carbonate treatment gave from this Krafft and Vorster's diphenyl selenium oxide, melting at 106–108°, and solution of the latter in dry benzene and saturation with hydrochloric acid, or simply treatment with concentrated hydrochloric acid, gave the dichloride, $(C_6H_5)_2SeCl_2$ (Table III). The last substance was unstable, beginning to decompose at 137° and melting at 142°. We have, therefore, an analogy for the reactions described in the foregoing paragraphs, equations for which may be written as follows.

$$C_6H_5SeR + 3HNO_3 = C_6H_5SeOR{\cdot}HNO_3 + 2NO_2 + H_2O \qquad \text{(I)}$$
$$2C_6H_5SeOR{\cdot}HNO_3 + Na_2CO_3 = 2C_6H_5SeOR + 2NaNO_3 + CO_2 + H_2O \qquad \text{(II)}$$
$$C_6H_5SeOR + 2HCl = C_6H_5SeCl_2R + H_2O \qquad \text{(III)}$$

The suggested mechanism for this last reaction is given under another heading.

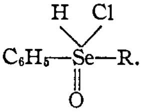
**The Action of Potassium Permanganate on the Seleno-Ethers.**—Methylphenyl, ethylphenyl, *iso*-amylphenyl and diphenyl selenides were dissolved in glacial acetic acid and oxidized at room temperature with a saturated aqueous solution containing one equivalent of potassium permanganate. No selenoxide except the diphenyl could be isolated by this process but by filtering, cooling the reaction mixture in ice and saturat-

TABLE IV

PREPARATION OF THE DICHLORIDES, $C_6H_5SeCl_2R$, BY THE ACTION OF $KMnO_4$ AND HCL ON THE SELENO-ETHERS

| R | Seleno-ether, g. | HAc, cc. | $KMnO_4$, g. | Yield, g. | Yield, % | Crystallizing solvent | M. p., °C. | Analysis for Cl Calcd. | Analysis for Cl Found |
|---|---|---|---|---|---|---|---|---|---|
| $CH_3$ | 20 | 100 | 12.2 | 18.6 | 68.5 | Xylene | 122<br>(dec.) | 29.3 | 29.1<br>29.6 |
| $C_2H_5$ | 10 | 50 | 3.7 | 2 | 13 | Ether | 64–65 | 27.7 | 27.8 |
| $C_5H_{11}$ | 6.3 | 33 | 2.3 | 6.3 | 76 | EtOH | 80 | 23.8 | 24.0 |
| $C_6H_5$ | 13.8 | 50 | 3.8 | 7.1 | 25 | Xylene | 142<br>(dec.) | 23.6 | 23.7<br>23.8 |

ing with hydrogen chloride there was precipitated in every case a white solid that could be filtered off and recrystallized. These white solids turned out to be the dichlorides described above. For the details of these procedures see Table IV.

The formation of such compounds is rather unexpected. They could not be formed by the direct action of chlorine produced from the oxidation of hydrochloric acid by the permanganate, because a spot test on filter paper was made in each case and the absence of free permanganate established before the hydrochloric acid was added. They must, therefore, have been formed by the action of the acid upon an intermediate oxidation product, in all probability the selenoxide. One would anticipate, from the behavior of nitric acid, the formation of hydrochlorides of the general formula,  $C_6H_5\text{—}\underset{\underset{O}{\|}}{\overset{H\ \ Cl}{\overset{\diagdown\diagup}{Se}}}\text{—}R$.

In order to prove their constitution we treated the methyl and phenyl seleno-ethers with dry chlorine, using dry ether as a solvent, and in each case obtained the same type of dichloride, $C_6H_5SeCl_2R$, that we had by the other methods.

$$C_6H_5SeR + Cl_2 = C_6H_5SeCl_2R \qquad \text{(IV)}$$

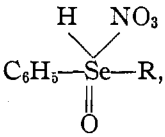
The ethyl and *iso*-amyl derivatives decomposed under the action of chlorine, evolving hydrochloric acid, so that their constitution could not be checked in the same way.

TABLE V

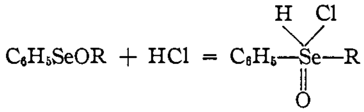
PREPARATION OF THE DICHLORIDES BY THE DIRECT ACTION OF CHLORINE ON THE SELENO-ETHERS

| R | Seleno-ether, g. | Yield, g. | Yield, % | Mixed m. p., °C. |
|---|---|---|---|---|
| $CH_3$ | 9 | 7 | 56.5 | 122 (dec.) |
| $C_6H_5$ | 15 | 16.5 | 84 | 142 (dec.) |

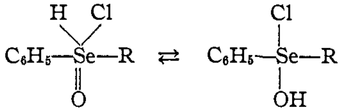
## Discussion of Results

Aromatic seleno-ethers differ from the corresponding sulfur compounds in that they do not oxidize readily to the hexavalent condition but, under similar conditions, produce compounds corresponding to the sulfoxides rather than to the sulfones. This is probably due to the fact that oxidized selenium in these compounds has certain basic characteristics, adding nitric acid readily to produce loose molecular compounds of the type,  $C_6H_5\text{—}\underset{\underset{O}{\|}}{\overset{H\ \ NO_3}{\overset{\diagdown\diagup}{Se}}}\text{—}R$, in which the selenium is hexavalent and further oxidation is impossible. By neutralizing the acid with a base, oxidation to the hexavalent state can then be carried to completion and selenones, $C_6H_5SeO_2R$, are obtained.[12] The acid addition products are evidently of the nature of salts, for they ionize readily in water solution to give the nitrate ion and presumably a positive ion, $(C_6H_5SeHOR)^+$.

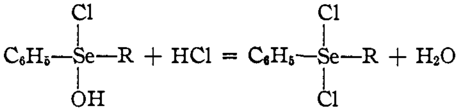
Hydrochloric acid does not form addition products but converts the selenoxides to dichlorides. In order to correlate this behavior with the addition of nitric acid to the oxides, we assume that an addition product with the hydrochloric acid first forms, but immediately rearranges to a tetravalent hydroxyl derivative, the hydroxyl group of which is then capable of reacting with another molecule of hydrochloric acid to form the dichloride.



$$C_6H_5SeOR + HCl = C_6H_5{-}\underset{\underset{O}{\|}}{\overset{H\;\;Cl}{\overset{\diagdown\diagup}{Se}}}{-}R \qquad (V)$$



$$C_6H_5{-}\underset{\underset{O}{\|}}{\overset{H\;\;Cl}{\overset{\diagdown\diagup}{Se}}}{-}R \rightleftarrows C_6H_5{-}\underset{\underset{OH}{|}}{\overset{\overset{Cl}{|}}{Se}}{-}R \qquad (VI)$$



$$C_6H_5{-}\underset{\underset{OH}{|}}{\overset{\overset{Cl}{|}}{Se}}{-}R + HCl = C_6H_5{-}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{Se}}{-}R + H_2O \qquad (VII)$$

The hydrochloric acid in the last reaction may even be obtained at the expense of a molecule of the original addition product, for diphenyl selenoxide, when recrystallized from concentrated hydrochloric acid, gave a product with no sharp melting point; this may well have been a mixture of the selenoxide and the dichloride, for it was readily converted completely to the dichloride by further treatment with concentrated hydrochloric acid.

The dichlorides also appear to be salts, ionizing readily in water solution.

## Summary

By the action of alkyl halides on sodium selenophenolate the authors have prepared two new and two known alkyl or aryl phenyl seleno-ethers. They have studied the action of several oxidizing agents upon these compounds and have prepared some nitric acid addition products of the oxides formed. The action of hydrochloric acid on the oxides has also been investigated, the constitution of the products proved and a mechanism for the reaction proposed.

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