[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

# ORGANIC COMPOUNDS OF SELENIUM. I. THE ACTION OF SELENIUM OXYCHLORIDE UPON KETONES

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Selenium oxychloride is a very reactive compound and, therefore, lends itself readily to the syntheses of organic selenium compounds. Its activity may be classified under three headings, chlorination, oxidation and condensation.

The action of selenium oxychloride on paraffins, olefins, acetylenes, ethers, phenols, tertiary aromatic amines, Grignard's reagent, ketones and aromatic hydrocarbons has been described more or less thoroughly in the literature.[1]

In this investigation selenium oxychloride was allowed to act on the following ketones: acetone, acetophenone, propiophenone, *p*-chloro-acetophenone, methyl *p*-tolyl ketone, 2-methyl-5-isopropylacetophenone, methyl *n*-hexyl ketone, methyl ethyl ketone, diethyl ketone and benzophenone In general, the reaction can be represented by $2C_6H_5COCH_3 + OSeCl_2 \longrightarrow (C_6H_5COCH_2)_2SeCl_2 + H_2O$.

The reactions were carried out at room temperature with the exception of 2-methyl 5-isopropyl ketone. In this case the reaction was accelerated by heat.

The products were nearly insoluble in ether, benzene, petroleum ether and carbon tetrachloride. They were soluble in both water and alcohol with decomposition. No satisfactory method of recrystallization was found and it was necessary to remove impurities by first washing with benzene and then with ether.

Diethyl, methyl ethyl and methyl *n*-hexyl ketone reacted violently with the generation of heat and the evolution of hydrogen chloride. The solvent turned yellow, and then red, due to the decomposition of either the selenium oxychloride or a new product, but no solid separated.

The products of the action of selenium oxychloride on the ketones are more or less unstable, some beginning decomposition at once and others not showing marked decomposition for a period of two weeks. Decomposition gives a reddish sticky mass with strong lachrymatory action and an odor like that of chloro ketones.

Some dichloroselenomethyl *p*-tolyl ketone was accidentally spilled on the investigator's hand. The skin became irritated and later formed slight

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[1] Morgan and Burstall, *J. Chem. Soc.*, **130**, 3260 (1928); Frick, THIS JOURNAL, **45**, 1795 (1923); Mueller, *Chem.-Ztg.*, **43**, 843 (1919); Lenher, THIS JOURNAL, **43**, 29 (1921); Kunckell, *Ber.*, **28**, 609 (1795); Michaelis and Kunckell, *ibid.*, **30**, 2823 (1897); Kunckell and Zimmermann, *Ann.*, **314**, 281 (1901); Strecker and Willing, *Ber.*, **48**, 196 (1915); Godchaux, *ibid.*, **24**, 765 (1891).

pockets that remained red for four days. Then the skin peeled off on the affected area as in the case of a sunburn.

## Experimental

The ketones used in the experiments were obtained from the Eastman Kodak Company. 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 the ratio of two moles of the ketone to one mole of the selenium oxychloride. Anhydrous ether was found to be the most satisfactory solvent in which to carry out the reactions. The mixture was rapidly stirred and usually in a few minutes a white solid separated with the generation of considerable heat.

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

Analysis for selenium[2] was carried out by fusion with potassium nitrate and sodium peroxide in a Parr bomb. The fused mass was dissolved, acidified with hydrochloric acid and the selenium precipitated by means of sulfur dioxide.

Analysis for chlorine was carried out in a similar way except that nitric acid was used for acidifying and silver chloride was precipitated by the addition of silver nitrate. The analyses indicate a certain amount of chlorination.

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

TABLE I

PREPARATIONAL DATA, PHYSICAL CONSTANTS AND ANALYSES

| | Ketone | Seleno product | Formula | M. p., °C. | Yield, % | Decomposition[a] | Selenium, % | | Chlorine, % | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Calcd. | Found | Calcd. | Found |
| 1 | Acetone | Dichloroseleno-acetone | $(CH_3COCH_2)_2SeCl_2$ | 81 | 77 | 3–4 Hours | 29.98 | 29.98 | 26.84 | 27.19 |
| 2 | Acetophenone | Dichloroseleno-acetophenone | $(C_6H_5COCH_2)_2SeCl_2$ | 121.5 | 77 | 1–2 Days | 20.41 | 20.02 | 18.27 | 18.25 |
| 3 | *p*-Chloro-acetophenone | Dichloroseleno-*p*-chloro-acetophenone | $(ClC_6H_4COCH_2)_2SeCl_2$ | 126 | 50 | 1–2 Weeks | 17.33 | 17.35 | 31.03 | 31.02 |
| 4 | Propiophenone | Dichloroselenopropiophenone | $(C_6H_5COC_2H_4)_2SeCl_2$ | 118 | 60 | 2 Weeks | 19.03 | 18.61 | 17.04 | 17.36 |
| 5 | Methyl *p*-tolyl ketone | Dichloroselenomethyl *p*-tolyl ketone | $(CH_3C_6H_4COCH_2)_2SeCl_2$ | 129 | 60 | 2 Weeks | 19.03 | 18.00 | 17.04 | 17.49 |
| 6 | 2-Methyl 5-isopropylacetophenone | Dichloroseleno-2-methyl-5-isopropylacetophenone | $[CH_3(C_3H_7)C_6H_3COCH_2]_2SeCl_2$ | 133 | 50 | 2 Weeks | 15.83 | 14.67 | 14.17 | 15.07 |

[a] Impurities apparently affect the stability considerably as different lots showed varying degrees of stability. Contact with an iron spatula frequently started decomposition at once.

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

Methyl *n*-hexyl ketone, methyl ethyl ketone and diethyl ketone reacted violently but produced no solid and the products seemed to decompose as fast as they were formed.

Benzophenone was treated with selenium oxychloride in carbon disulfide solution in the presence of anhydrous aluminum chloride and heated for several days. Hydrogen chloride was given off slowly. After standing for two weeks, most of the solvent evaporated, leaving a crystalline mass. It was extracted with chloroform and on the evaporation of the chloroform crystals separated. They were placed on a porous plate but decomposed as soon as the protecting layer of chloroform evaporated.

## Summary

1. The reaction between selenium oxychloride and certain ketones has been studied.

2. Condensation reactions took place between two molecules of the ketones and one molecule of selenium oxychloride.

3. New organic compounds of selenium have been prepared and studied.

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[Contribution from the Chemical Laboratory of Harvard University]

# CYCLIC NITRONES

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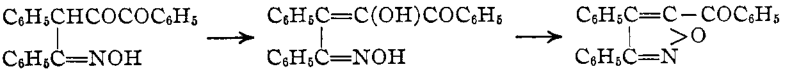
In earlier papers of this series there is mention of a "purple anhydride" which appeared in small quantities whenever solutions of triphenyl butane trione oxime became acid. Like benzoyl diphenyl isoxazole, previously investigated, this purple compound is a monomolecular anhydride of the oxime. It is, therefore, a surprisingly simple compound to have such a rich, deep purple color. This wide contrast between color and complexity was one of the reasons for the investigation.

Another incentive for investigating the purple compound arose from the difficulty of accounting for more than one monomolecular anhydride. The oxime is so constituted as to make an open-chained anhydride impossible, and the evidence is conclusive that the isoxazole derivative represents the anhydride of the only possible enolic modification of the open-chained oxime



$$\begin{array}{l} C_6H_5CHCOCOC_6H_5 \\ \quad | \\ C_6H_5C{=}NOH \end{array} \longrightarrow \begin{array}{l} C_6H_5C{=}C(OH)COC_6H_5 \\ \quad | \\ C_6H_5C{=}NOH \end{array} \longrightarrow \begin{array}{l} C_6H_5C{=}C-COC_6H_5 \\ \quad |\quad\ >O \\ C_6H_5C{=}N \end{array}$$

In view of these facts it seemed probable that the formation of the purple compound is preceded by a rearrangement of the oxime. Since the slightest imaginable acidity leads to the appearance of the substance, a rearrangement involving the carbon chain is unlikely, but an interchange