CHLORINATION OF KETONES WITH
SELENIUM OXYCHLORIDE

by

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ABSTRACT

A new method of synthesizing α -haloketones was developed by reacting selenium oxychloride or selenium oxybromide with ketones possessing an active methylene group. The rate of formation of the dichloroselenoketone is aided by an electron-donating group in the para position of the benzene ring while hindered by an electron-withdrawing group in the para position. The decomposition of the dichloroselenoketone leads to the α -chloroketone. The use of selenium oxybromide leads directly to the α -bromoketone without isolation of a dibromoselenoketone.

PREPARATION AND PROPERTIES

1. Selenium Oxychloride

Selenium oxychloride, SeOCl_2 , was first synthesized in 1859 by Weber,¹ who brought together the vapors of selenium tetrachloride and selenium dioxide. In 1887 Michaëlis² prepared selenium oxychloride by the interaction of phosphorus pentachloride upon selenium dioxide. A short time later Cameron and Macallan³ allowed a mixture of selenium dioxide and sodium chloride to interact and obtained sodium selenite and selenium oxychloride.

The research of Lenher⁴ during the early 1920's led to three different methods of preparing selenium oxychloride. They are as follows: direct union of selenium tetrachloride and selenium dioxide at room temperature; partial hydrolysis of selenium tetrachloride; and dehydration of dichloroselenious acid, $\text{SeO}_2 \cdot 2\text{HCl}$. A laboratory preparation based on the ideas of Lenher is found in "Inorganic Synthesis."⁵

The physical properties of selenium oxychloride have been investigated by Lenher.^{6,7,8,9} Selenium oxychloride is a pale yellow liquid that boils at 176.4° at 726 mm., melts at 8.5° , D_4^{22} 2.424, and n_D^{20} 1.6516. In moist air selenium oxychloride fumes, liberating hydrochloric acid. Near the

boiling point under atmospheric conditions selenium oxychloride partially decomposes forming selenium dioxide, selenium tetrachloride, and selenium. Selenium oxychloride is miscible in all proportions forming physical mixtures with benzene, carbon disulfide, carbon tetrachloride, and chloroform. When 0.005 ml. of selenium oxychloride is applied to the skin of a man,¹⁰ a third degree burn is produced which takes nearly 30 days to heal.

The chemical properties of selenium oxychloride were first examined by Lenher^{6,7} who investigated the action upon naturally occurring materials such as wood, leather, resins, carbohydrates, proteins, etc., in addition to most inorganic elements and compounds. He noted that selenium oxychloride is a very powerful oxidizing and chlorinating agent. The chemical action of selenium oxychloride upon alcohols,^{11,12} tertiary aromatic amines,^{13,14,15} esters,¹⁶ ethers,^{17,18} Grignard's reagent,¹⁹ ketones^{20,21,22} olefins,^{6,23,24,25} and phenols^{18,26,27} has been described in the literature. With ketones, selenium tetrachloride^{18,26,28,29} forms the same selenium adduct as does selenium oxychloride.

2. Selenium Oxybromide

Selenium oxybromide, SeOBr_2 , was first synthesized in 1866 by Schneider,³⁰ who reacted selenium dioxide with selenium tetrabromide. In 1913 Glauser³¹ prepared selenium

oxybromide by allowing sodium bromide to interact with selenium oxychloride. Lenher,³² in 1922, modified Schneider's method by mixing selenium with selenium dioxide and then adding bromine. Just recently Klikorka³³ prepared selenium oxybromide by treating aluminum bromide with selenium oxychloride.

Lenher³² has described the physical and chemical properties of selenium oxybromide. It is a reddish-yellow solid that melts at 41.6° and boils at 216° at 740 mm. with considerable decomposition. Selenium oxybromide is readily soluble in benzene, carbon disulfide, chloroform, toluene, and xylene. The chemical properties are very similar to those of selenium oxychloride.

3. Selenium Tetrachloride

In 1818 Berzelius³⁴ passed the vapors of chlorine over elemental selenium which is converted to diselenium dichloride, Se_2Cl_2 , which then combines with more chlorine to form selenium tetrachloride, SeCl_4 . Michaelis,^{35,36} in 1871, reacted selenium oxychloride with phosphorus oxychloride or selenium with thionyl chloride to prepare selenium tetrachloride. A short time later Clausnizer^{37,38} interacted selenium with sulfuryl chloride or selenium oxychloride with sulfuryl chloride to synthesize selenium tetrachloride. Lenher and North³⁹ prepared selenium tetrachloride in 1907 using selenium oxychloride and thionyl chloride.

Selenium tetrachloride is a bright yellow crystalline solid that sublimates at $196 \pm 1^\circ$ and melts at $305 \pm 3^\circ$.⁴⁰ From 109 to 226° ,⁴¹ the vapors from selenium tetrachloride consist entirely of selenium dichloride, SeCl_2 , and chlorine. Selenium tetrachloride is slightly soluble in alcohol, carbon tetrachloride, chloroform, and ether.

Selenium tetrachloride reacts with many elements and inorganic compounds. The chemical action of selenium tetrachloride upon acids,^{42,43} amines,^{14,44,45} esters,⁴³ Grignard's reagent,⁴⁶ ketones,^{18,26,28,29,47,48,49} and olefins^{50,51,52,53,54} has been described in the literature.

DISCUSSION

A new method for synthesizing α -halo ketones in yields of 24-63% (Table I) was developed by reacting selenium oxychloride or selenium oxybromide with ketones possessing an active methylene group. The general reactions can be represented by the following equations:

It was possible using selenium oxychloride to isolate the dichloroselenoketone in yields of 43-87% (Table I). with each ketone except methyl ethyl ketone. The solid selenium adduct usually remains stable from one to two weeks with the exception of those formed from acetone and cyclohexanone which start to decompose shortly after formation. When the dichloroselenoketone is decomposed by heating with a free flame or warming slowly in a mineral oil bath, hydrochloric acid is evolved below the melting point. After purification,

TABLE I
PERCENTAGE YIELDS

	Dichloroseleno-	Selenium	α -Chloro-
Acetophenone	57.8-79.4	89.1-96.0	33.6-49.5
p-Bromoacetophenone	42.9-46.8	40.2	38.6
p-Methoxyacetophenone	63.8-86.5	97.7	40.6
p-Methylacetophenone	69.3	93.6	38.7
Propiophenone	46.4-52.3	81.3-81.8	25.6-41.6
Methyl t-butyl ketone	69.4	69.6	45.7
Acetone	82.7	71.8-86.2	24.1-37.1
Methyl ethyl ketone	---	88.2	29.8-34.5
Cyclohexanone	---	91.3	39.1-40.8
	Dibromoseleno-	Selenium	α -Bromo-
Acetophenone	---	---	48.7-62.7
Methyl t-butyl ketone	---	---	46.1
Cyclohexanone	---	---	30.8

a vacuum distillation of the residue leads to α -chloroketone, a small amount of the starting ketone, and a fair amount of tar.

The observed infrared and ultraviolet spectrum of the carbonyl for the various ketones, α -chloroketones, and dichloroselenoketones are listed on page 8 and 9, respectively.

In order to determine the relative effects of groups substituted in the para position of the benzene ring, a rate study was performed in which each ketone was mixed in equimolar quantities with acetophenone, which was in 10 mole excess of the selenium oxychloride used. The dichloroselenoketone was reduced by sodium borohydride to the α -arylethanol. The relative rates compared to α -phenylethanol are as follows:

1.00

0.78

1.36

5.34

TABLE II

OBSERVED INFRARED MAXIMA FOR THE CARBONYL
(Frequency of Absorption Bands in cm.^{-1})^a

		α -Chloro-	Dichloroseleno-
Acetophenone	1688	1700, 1680	1663
p-Bromoacetophenone	1685	1720, 1698	1663
p-Methoxyacetophenone	1677	1714, 1693	1655, 1645
p-Methylacetophenone	1670	1695, 1675	1648
Propiophenone	1677	1695	1650
Methyl t-butyl ketone	1712	1700	
Acetone	1700	1710, 1677	
Methyl ethyl ketone	1700	1710	
Cyclohexanone	1700	1710, 1677	

^aAll of the spectra were obtained using a Perkin-Elmer Infracord double beam spectrophotometer with sodium chloride prisms. The spectra of all the liquid and solid ketones were obtained using carbon tetrachloride as the solvent, while the solid dichloroselenoketones were determined in potassium bromide pellets.

TABLE III
OBSERVED ULTRAVIOLET SPECTRAL DATA FOR THE CARBONYL
(λ_{max} is in Å)^a

		α -Chloro-	Dichloroseleno-
Acetophenone	2430	2470	2485
p-Bromoacetophenone	2550	2580	2635
p-Methoxyacetophenone	2740	2810	2850, 2895
p-Methylacetophenone	2545	2575	2625
Propiophenone	2420	2450	2540

^aAll of the spectra were determined in 95% ethyl alcohol using the Model 11 Cary recording ultraviolet spectrophotometer.

Thus an electron donating group in the para position increases the rate of reaction while an electron withdrawing group decreases the reaction rate.

No dibromoselenoketone was ever isolated using selenium oxybromide. It has been reported by Kunckell and Zimmermann⁵⁵ that the addition of bromine to selenoacetophenone, $(\text{C}_6\text{H}_5\text{COCH}_2)_2\text{Se}$, formed the white dibromoselenoacetophenone, m.p. 97° .

EXPERIMENTAL^a

1. Selenium Oxychloride Chlorinations

a. Selenium Oxychloride

The selenium oxychloride was obtained from the J. T. Baker Chemical Company and was not further purified.

b. Dichloroselenoacetophenone

In a 500-ml., round-bottom flask was placed a cold solution of 48.2 gm. (0.4 mole) of acetophenone, b.p. 197-199° (lit.⁵⁶ b.p. 202°), n_D^{28} 1.5302 (lit.⁵⁷ $n_D^{20.7}$ 1.5336), dissolved in 200 ml. of ether which was protected by a calcium chloride drying tube. To this was added a solution of 33.2 gm. (0.2 mole) of selenium oxychloride in 50 ml. of ether. The reaction mixture was occasionally swirled while being cooled in an ice-bath to moderate the exothermic reaction. During the course of the reaction the color of the solution changed from light yellow to deep yellow or to dark red depending upon the amount of solvent present.

After two hours the reaction mixture was filtered by suction to collect the desired precipitate which was washed with fresh solvent and dried. The white dichloroselenoacetophenone weighed 54.1 gm. (70.3%), m.p. 120° (lit.⁵⁸ m.p. 121.5°).

^aAll melting and boiling points are uncorrected.

c. α -Chloroacetophenone

With a free flame, 25.0 gm. of solid dichloroselenoacetophenone was gently heated in air. During the initial melting process white fumes of hydrochloric acid were evolved while the solution turned black. On further heating for an hour at 150-200° the solution deposited some solid and more hydrochloric acid was evolved.

After cooling, the liquid residue was decanted from the black precipitate which was then washed with three 25-ml. portions of ether. There was recovered 4.85 gm. (95.4%) of black selenium metal. The combined ether washes were added to the decanted residue, filtered, and dried with anhydrous magnesium sulfate. Evaporation of the ether followed by a vacuum distillation of the residue at 7 mm. led to three fractions: "a" 0.90 gm. of a colorless liquid, b.p. 70-80°; "b" 1.90 gm. of a colorless liquid and a white solid, b.p. 80-100°; and "c" 7.10 gm. of a white solid, b.p. 105-117°.

The products from the vacuum distillation were analyzed and characterized by the following techniques. A vapor phase chromatography (V.P.C.) analysis of "a" showed it to be pure acetophenone, n_D^{28} 1.5322 (lit.⁵⁷ $n_D^{20.7}$ 1.5336) while "b" consisted of 65% acetophenone and 35% α -chloroacetophenone, n_D^{28} 1.5394. The melting point of "c" was 56° (lit.⁵⁹ m.p. 58°). A positive Beilstein test⁶⁰ for halogen was obtained from "c" and in the presence of a saturated solution of sodium iodide in acetone,⁶¹ sodium chloride was deposited. The 2,4-dinitrophenylhydrazone of "c" melted at 218° (lit.⁶⁵ m.p. 214-215°).

The infrared spectrum of "a" showed absorption maximum for the carbonyl at 1685 cm.^{-1} (lit.⁶² 1692 cm.^{-1}) while "c" showed carbonyl peaks at 1700 and 1680 cm.^{-1} (lit.⁶³ 1704 and 1682 cm.^{-1}). There was recovered 7.75 gm. (38.9%) of α -chloroacetophenone (lit.⁶⁴ b.p. 140° at 15 mm.).

In an attempt to increase the yield of α -chloroacetophenone the following techniques were tried. In a 250-ml. , round-bottom flask was placed a cold solution of 24.1 gm. (0.2 mole) of acetophenone dissolved in 100 ml. of p-xylene which was protected by a calcium chloride drying tube. To this was added 16.6 gm. (0.1 mole) of selenium oxychloride in 25 ml. of p-xylene. The reaction mixture was swirled occasionally in an ice bath and then allowed to stand for three hours during which crystalline dichloroselenoacetophenone formed.

The entire contents of the flask were refluxed for 24 hours while the water which formed was removed from the mixture by means of a Dean-Stark apparatus. The liquid residue was decanted from the black precipitate which was then washed with three 25-ml. portions of ether. There was recovered 5.65 gm. (71.5%) of selenium. The organic layers were combined and the solvents were evaporated.

The liquid residue was vacuum distilled at 2.5 mm. and led to three fractions: "a" 2.54 gm. of a colorless liquid, b.p. $50\text{-}57^\circ$; "b" 5.14 gm. of a colorless liquid and a white solid, b.p. $57\text{-}92^\circ$, and "c" 0.84 gm. of a white solid, b.p. $93\text{-}96^\circ$. The V.P.C. analysis of "a" showed it to be pure

acetophenone, while "b" consisted of 40% acetophenone and 60% α -chloroacetophenone. There was recovered 3.93 gm. (12.7%) of α -chloroacetophenone.

In another effort to increase the yield of α -chloroacetophenone, 38.8 gm. (0.1 mole) of dichloroselenoacetophenone was placed in a large test tube and slowly warmed in a mineral oil bath. At 50° fumes of hydrochloric acid started to evolve; at 120°, the entire mixture liquified and more hydrochloric acid was evolved. The reaction mixture was kept for an hour at 175°.

The liquid residue was decanted from the black solid and washed with three 25-ml. portions of ether. There remained 7.6 gm. (96.3%) of selenium. The combined ether washes were added to the decanted residue, filtered, and dried with anhydrous magnesium sulfate. Evaporation of the ether left 24.4 gm. (78% of the theoretical α -chloroacetophenone) of liquid. A vacuum distillation of the residue at 1 mm. led to two fractions: "a" 3.7 gm. of a colorless liquid, acetophenone, b.p. 54-70°; "b" 15.3 gm. (49.5%) of a white solid, α -chloroacetophenone, b.p. 71-92°; and "c" 5.4 gm. of tar.

dd. p-Bromo- α -chloroacetophenone

From 79.6 gm. (0.4 mole) of p-bromoacetophenone, m.p. 50° (lit.⁶⁶ m.p. 51°) and 33.2 gm. (0.2 mole) of selenium oxychloride, 46.8 gm. (42.9%) of white dichloroseleno-p-bromoacetophenone, m.p. 125°, was obtained.

The decomposition of 33.0 gm. of dichloroseleno-p-bromoacetophenone led to a recovery of 1.92 gm. (40.2%) of black selenium. A vacuum distillation of the residue led to 10.9 gm. (38.6%) of a yellow-white solid, p-bromo- α -chloroacetophenone, b.p. 115-140° at 5 mm., m.p. 115° (lit.⁶⁷ m.p. 117-118°).

e. p-Methoxy- α -chloroacetophenone

From 30.0 gm. (0.2 mole) of p-methoxyacetophenone, m.p. 38° (lit.⁶⁸ m.p. 38-39°), and 16.6 gm. (0.1 mole) of selenium oxychloride, 38.2 gm. (86.5%) of white dichloroseleno-p-methoxyacetophenone, m.p. 120° (lit.⁶⁹ m.p. 122°) was obtained.

The decomposition of 32.0 gm. of dichloroseleno-p-methoxyacetophenone led to a recovery of 5.5 gm. (97.7%) of black metallic selenium. A vacuum distillation of the residue led to 10.7 gm. (40.6%) of a white solid, p-methoxy- α -chloroacetophenone, b.p. 150-175° at 8 mm. (lit.⁷⁰ b.p. 179-181° at 16-18 mm.), m.p. 101° (lit.⁷¹ m.p. 102°).

f. p-Methyl- α -chloroacetophenone

From 26.8 gm. (0.2 mole) of p-methylacetophenone, b.p. 218-221° (lit.⁷² b.p. 220°), n_D^{27} 1.5298 (lit.⁷³ n_D^{20} 1.5335), and 16.6 gm. (0.1 mole) of selenium oxychloride, 28.8 gm. (69.3%) of white dichloroseleno-p-methylacetophenone, m.p. 128° (lit.⁵⁸ m.p. 129°), was obtained.

The decomposition of 18.0 gm. of dichloroseleno-p-methylacetophenone led to a recovery of 3.2 gm. (93.6%) of black metallic selenium. A vacuum distillation of the residue led to two fractions: "a" 2.9 gm. of a colorless liquid, p-methylacetophenone, b.p. 95-135° at 8 mm., n_D^{27} 1.5347 (lit.⁷³ b.p. 93.5° at 7 mm., n_D^{20} 1.5335); and "b" 5.6 gm. (38.7%) of a white solid, p-methyl- α -chloroacetophenone, b.p. 135-145° at 8 mm., m.p. 54° (lit.⁷⁴ m.p. 55-56°).

g. α -Chloropropiophenone

From 26.8 gm. (0.2 mole) of propiophenone, b.p. 213-216° (lit.⁷⁵ b.p. 217°), n_D^{32} 1.5211 (lit.⁷⁶ n_D^{20} 1.5270), and 16.6 gm. (0.1 mole) of selenium oxychloride, 19.3 gm. (46.4%) of white dichloroselenopropiophenone, m.p. 122° (lit.⁷⁷ m.p. 124°), was obtained.

The decomposition of 11.0 gm. of dichloroselenopropiophenone led to a recovery of 1.7 gm. (71.8%) of black metallic selenium. A vacuum distillation of the residue led to 3.7 gm. (41.6%) of a yellow liquid, α -chloropropiophenone, b.p. 104-116° at 9 mm., n_D^{28} 1.5340 (lit.⁷⁸ b.p. 123-125° at 17 mm., n_D^{25} 1.5402).

h. 3,3-Dimethyl-1-chloro-2-butanone

From 20.0 gm. (0.2 mole) of methyl t-butyl ketone, b.p. 101-103° (lit.⁷⁹ b.p. 105°), n_D^{31} 1.3909 (lit.⁸⁰ n_D^{25}

1.3944), and 16.6 gm. (0.1 mole) of selenium oxychloride, 24.1 gm. (69.4%) of white dichloroseleno-methyl t-butyl ketone, m.p. 122° , was obtained.

The decomposition of 24.1 gm. of dichloroseleno-methyl t-butyl ketone led to a recovery of 3.8 gm. (69.6%) of black selenium. A vacuum distillation of the residue led to 8.5 gm. (45.7%) of a yellow liquid, 3,3-dimethyl-1-chloro-2-butanone, b.p. $47-51^{\circ}$ at 2 mm., n_D^{31} 1.4358 (lit.⁸¹ b.p. $75-76^{\circ}$ at 15 mm., n_D^{20} 1.4422).

i. Chloroacetone

From 11.6 gm. (0.2 mole) of acetone, b.p. 54° (lit.⁸² b.p. $56.2-56.3^{\circ}$), n_D^{27} 1.3558 (lit.⁸³ n_D^{25} 1.35695), and 16.6 gm. (0.1 mole) of selenium oxychloride, 21.8 gm. (82.7%) of a white solid dichloroselenoacetone, m.p. 84° (lit.⁸⁴ m.p. 82°), was obtained.

The decomposition of 20.0 gm. of dichloroselenoacetone led to a recovery of 4.3 gm. (71.8%) of black selenium. Distillation of the residue led to 5.45 gm. (37.1%) of chloroacetone, a colorless liquid, b.p. $114-120^{\circ}$ (lit.⁸⁵ b.p. 119°), n_D^{26} 1.4317 (lit.⁸⁶ $n_D^{19.5}$ 1.4340).

j. 3-Chloro-2-butanone

In a 250-ml. round-bottom flask was placed a solution of 14.4 gm. (0.2 mole) of methyl ethyl ketone, b.p. $76-77^{\circ}$, n_D^{27} 1.3758 (lit.⁸⁷ b.p. 79.5° , n_D^{25} 1.3761), in 100 ml. of

ether cooled in a Dry Ice-acetone slush which was protected by a calcium chloride drying tube. To this was added a solution of 16.6 gm. (0.1 mole) of selenium oxychloride in 25 ml. of ether. After a couple of hours the colorless solution turned from yellow to red while being swirled occasionally in an ice bath. It was found best to allow this mixture to stand for a few days so that all the red amorphous selenium could deposit itself.

The liquid residue was decanted from the red solid which was then washed with three 25-ml. portions of ether. There remained 6.95 gm. (88.2%) of red selenium. The combined ether washes were added to the decanted residue, filtered, and dried with anhydrous magnesium sulfate. Evaporation of the ether followed by a distillation of the residue led to 7.35 gm. (34.5%) of a yellow liquid, 3-chloro-2-butanone, b.p. 110-117° (lit.⁸⁸ b.p. 114-115°), n_D^{27} 1.4185 (lit.⁸⁹ n_D^{20} 1.4171).

k. 2-Chlorocyclohexanone

In a 250-ml. round-bottom flask was placed a cold solution of 19.6 gm. (0.2 mole) of cyclohexanone, b.p. 151-152° (lit.⁹⁰ b.p. 155.6-155.7°), n_D^{25} 1.4481 (lit.⁹¹ n_D^{16} 1.4521), in 100 ml. of ether which was protected by a calcium chloride drying tube. To this was added a solution of 16.6 gm. (0.1 mole) of selenium oxychloride in 25 ml. of ether over a period

of two minutes. The reaction mixture was frequently swirled in an ice bath to moderate the exothermic reaction. During the course of the reaction the color of the solution changed from light yellow to deep red.

The ether was evaporated and the residue gently heated in air with a free flame for an hour. The liquid residue was decanted from the red amorphous selenium and then washed with three 25-ml. portions of ether. The combined ether washes were added to the decanted residue, filtered, and dried with anhydrous magnesium sulfate. Evaporation of the ether followed by a vacuum distillation of the residue at 3 mm. led to three fractions: "a" 1.13 gm. of a colorless liquid, b.p. 38-50°, n_D^{29} 1.4537; "b" 0.524 gm. of a colorless liquid, b.p. 57-70°, n_D^{29} 1.4751; and "c" 7.46 gm. of a colorless liquid, b.p. 71-93°, n_D^{29} 1.4818. The V.P.C. analysis showed "a" was pure cyclohexanone (lit.⁹¹ b.p. 47° at 15 mm., $n_D^{16.9}$ 1.4521), "b" consisted of 60% cyclohexanone and 40% 2-chlorocyclohexanone, and "c" was pure 2-chlorocyclohexanone (lit.⁹² b.p. 78-78.5° at 7 mm., n_D^{20} 1.4831). There was recovered 10.85 gm. (40.8%) of 2-chlorocyclohexanone.

In a 500-ml. round-bottom flask was placed a solution of 19.6 gm. (0.2 mole) of cyclohexanone dissolved in 150 ml. of ether which was protected by a calcium chloride drying tube. To this was added a solution of 16.6 gm. (0.1 mole) of selenium oxychloride in 25 ml. of ether while the flask

was cooled in a Dry Ice-acetone slush bath. After a few minutes of swirling in an ice bath a whitish-yellow solid precipitated out of solution. Most of the solid was a homogeneous mass that could not be broken up; however, a few white crystals of dichloroselenocyclohexanone were isolated, m.p. 46° . After an hour at room temperature red selenium started to deposit out of the homogeneous mass. The reaction mixture was allowed to remain undisturbed for a few days so that all the selenium could deposit itself out of solution.

The liquid residue was decanted off from the red solid which was then washed with three 25-ml. portions of ether. There was recovered 7.2 gm. (91.3%) of red amorphous selenium. The combined ether washes were added to the decanted residue, filtered, and dried with anhydrous magnesium sulfate. Evaporation of the ether followed by a vacuum distillation of the residue at 2 mm. led to two fractions: "a" 1.6 gm. of a colorless liquid, b.p. $40-50^{\circ}$, n_D^{26} 1.4602; and "b" 9.8 gm. of a colorless liquid, b.p. $50-56^{\circ}$, n_D^{26} 1.4787. The V.P.C. analysis showed "a" consisted of 60% cyclohexanone and 40% 2-chlorocyclohexanone while "b" was pure 2-chlorocyclohexanone. There was recovered 10.34 gm. (39.1%) of 2-chlorocyclohexanone.

TABLE IV
PREPARATIONAL DATA AND MELTING POINTS

Ketone	Dichloroseleno- Formula	Melting Point
Acetophenone	$(C_6H_5COCH_2)_2SeCl_2$	120°
p-Bromoacetophenone	$(BrC_6H_4COCH_2)_2SeCl_2$	125°
p-Methoxyacetophenone	$(CH_3OC_6H_4COCH_2)_2SeCl_2$	120°
p-Methylacetophenone	$(CH_3C_6H_4COCH_2)_2SeCl_2$	128°
Propiophenone	$(C_6H_5COC_2H_5)_2SeCl_2$	124°
Methyl t-butyl ketone	$(C_4H_9COCH_2)_2SeCl_2$	122°
Acetone	$(CH_3COCH_2)_2SeCl_2$	84°
Cyclohexanone	$(C_6H_{11}CO)_2SeCl_2$	46°

2. Selenium Oxybromide Brominations

a. Selenium Oxybromide

To prepare selenium oxybromide,³² commercial selenium dioxide was purified by adding a few drops of fuming nitric acid and gently heating with a free flame until the selenium dioxide sublimed into long white needles. There was ground together in a mortar 5.50 gm. (0.05 mole) of selenium dioxide with 3.98 gm. (0.05 mole) of black powdered selenium and the solid mixture was then placed in a 200-ml. round-bottom flask to which was attached a dropping funnel containing 15.98 gm. (0.1 mole) of bromine. The flask was surrounded by an ice bath in order to moderate the exothermic reaction. After all the bromine had been added, the mixture of selenium tetrabromide and selenium dioxide was warmed for an hour on a water bath at 40-50° forming selenium oxybromide as a liquid orange-brown mass.

b. α -Bromoacetophenone

To the cooled selenium oxybromide was added 24.1 gm. (0.2 mole) of acetophenone in 25 ml. of ether. The heterogeneous mixture was warmed on a water bath at 30-35° until a homogeneous solution formed. The reaction mixture was briefly cooled in an ice bath and after a few minutes fine white grain crystals formed which were identified as selenium dioxide. Five hours later solid black selenium

began to precipitate out of solution. The reaction mixture was left undisturbed overnight.

The following day, the liquid residue was decanted and two 25 ml. portions of ether were used to wash the black and white solid. The combined ether washes were added to the black liquid residue; the solution was filtered three times resulting in a pale yellow solution. There was recovered 24.95 gm. (62.7%) of α -bromoacetophenone by a water vacuum distillation of the ether.

The product, α -bromoacetophenone, was identified by employing the following techniques. The white solid melted at 52° (lit.⁹³ m.p. 50°). A mixed melting point with an authentic sample did not depress the melting point. A positive Beilstein test⁶⁰ for halogen was obtained and in the presence of a saturated solution of sodium iodide in acetone,⁶¹ sodium bromide was deposited. The infrared spectrum showed absorption maximum for the carbonyl at 1690 and 1675 cm.⁻¹.

c. 3,3-Dimethyl-1-bromo-2-butanone

To the solid selenium oxybromide was added 20.0 gm. (0.2 mole) of pinacolone. The same procedure was followed as with acetophenone except that upon the evaporation of the ether a liquid residue remained. A vacuum distillation of the residue led to 16.45 gm. (46.1%) of 3,3-dimethyl-1-bromo-2-butanone, a yellow liquid, b.p. 45-51° at 1.5 mm., n_D^{23} 1.4693 (lit.⁹⁴ b.p. 59° at 4 mm., n_D^{25} 1.4659).

d. 2-Bromocyclohexanone

To the solid selenium oxybromide was added 19.6 gm. (0.2 mole) of cyclohexanone. The same procedure was followed as with pinacolone. A vacuum distillation of the liquid residue at 7 mm. led to three fractions: "a" 1.19 gm. of a clear liquid, b.p. 30-50°, n_D^{24} 1.4844; "b" 3.46 gm. of a pale yellow liquid, b.p. 50-65°, n_D^{24} 1.5022; "c" 7.55 gm. of a yellow liquid, b.p. 65-78°, n_D^{24} 1.5115. The V.P.C. analysis of "a" showed 80% cyclohexanone (lit.⁹¹ b.p. 47° at 15 mm., $n_D^{16.9}$ 1.4521) and 20% 2-bromocyclohexanone, "b" consisted of 10% cyclohexanone and 90% 2-bromocyclohexanone, and "c" consisted of pure 2-bromocyclohexanone (lit.⁹⁵ b.p. 112-113° at 20 mm., n_D^{25} 1.5085). There was recovered 10.9 gm. (30.8%) of 2-bromocyclohexanone.

3. Selenium Tetrachloride Chlorination

a. Selenium Tetrachloride

In a 45-cm. long Pyrex tube having an inside diameter of 25 mm. was placed 15.9 gm. (0.2 mole) of black powdered selenium. Chlorine was generated by dripping concentrated hydrochloric acid on potassium permanganate and allowing the vapors to first pass through concentrated sulfuric acid. Diselenium dichloride formed almost immediately with the evolution of heat. Gentle heating with a microburner for about one hour led to 35.6 gm. (79.6%) of yellow crystalline selenium tetrachloride.

b. Dichloroselenoacetophenone

In a 500-ml. round-bottom flask was placed a cold solution of 36.1 gm. (0.3 mole) of acetophenone dissolved in 800 ml. of ether. To this was added 33.1 gm. (0.15 mole) of selenium tetrachloride and the mixture magnetically stirred for two hours. After filtering and drying 35.8 gm. (61.6%) of white dichloroselenoacetophenone, m.p. 120°, was recovered.

c. α -Chloroacetophenone

In a large test tube 32.0 gm. (0.0825 mole) of dichloroselenoacetophenone was heated in a mineral oil bath for one hour at 175° during which fumes of hydrochloric acid were given off. The liquid residue was decanted with ether leaving behind 6.3 gm. (96.8%) of selenium. Evaporation of the ether left 20.1 gm. (79.8% of the theoretical α -chloroacetophenone) of liquid. A vacuum distillation of the residue at 1.5 mm. led to two fractions: "a" 0.9 gm. of a colorless liquid, acetophenone, b.p. 59-73°; "b" 12.5 gm. (49.1%) of a white solid, α -chloroacetophenone, b.p. 74-92°; and "c" 6.7 gm. of tar.

4. Sodium Borohydride Reductions

a. α -Phenylethanol (from acetophenone)

In a 250-ml. round-bottom flask was added 12.0 gm. (0.1 mole) of acetophenone dissolved in 100 ml. of absolute ethanol; to this was added 1.25 gm. (0.033 mole) of sodium

borohydride, a slight excess. The reaction mixture was heated on a water bath at 90-100° until most of the ethanol had evaporated. The remaining liquid was extracted with 100 ml. of ether which was added to a separatory funnel containing 100 ml. of water. The upper ether layer was extracted, filtered, and dried with anhydrous magnesium sulfate. After evaporation of the ether a distillation of the residue led to 10.3 gm. (85.8%) of a colorless liquid, α -phenylethanol, b.p. 195-198° (lit.⁹⁶ b.p. 202-204°), n_D^{22} 1.5262 (lit.⁹⁷ 1.5244). The N-phenylcarbamate derivative melted at 91° (lit.⁹⁸ m.p. 92°).

b. α -Phenylethanol (from dichloroselenoacetophenone)

In a 500-ml. round-bottom flask was added 7.75 gm. (0.02 mole) of dichloroselenoacetophenone in 200 ml. of absolute alcohol. The reaction mixture was refluxed until all the solid dissolved; as excess sodium borohydride, 2.0 gm., was added, the solution turned red as selenium began to deposit out and colorless as selenium was further reduced. The reaction mixture was heated on a water bath at 90-100° until most of the alcohol evaporated. The remaining liquid was extracted with 100 ml. of ether which was added to a separatory funnel containing 100 ml. of water. The upper ether layer was extracted and dried with anhydrous magnesium sulfate. After evaporation of the ether a vacuum distillation

of the residue led to 3.56 gm. (80.8%) of a colorless liquid, α -phenylethanol, b.p. 84-97° at 8 mm. (lit.⁹⁹ b.p. 85-86° at 7 mm.), n_D^{25} 1.5242 (lit.⁹⁷ n_D^{25} 1.5244).

c. p-Bromophenyl- α -ethanol

From 19.9 gm. (0.1 mole) of p-bromoacetophenone and 1.25 gm. (0.033 mole) of sodium borohydride, 15.9 gm. (79.8%) of a colorless liquid, p-bromophenyl- α -ethanol, b.p. 125-128° at 8 mm., (lit.¹⁰⁰ b.p. 133-134° at 15 mm.), n_D^{28} 1.5651 (lit.¹⁰¹ n_D^{18} 1.5740), was obtained after a vacuum distillation of the residue.

d. p-Methoxyphenyl- α -ethanol

From 15.0 gm. (0.1 mole) of p-methoxyacetophenone and 1.25 gm. (0.033 mole) of sodium borohydride, 11.7 gm. (77.9%) of a colorless liquid, p-methoxyphenyl- α -ethanol, b.p. 122-125° at 8 mm. (lit.¹⁰² b.p. 110° at 13 mm.), n_D^{26} 1.5313, was obtained after a vacuum distillation of the residue.

e. p-Methylphenyl- α -ethanol

From 13.4 gm. (0.1 mole) of p-methylacetophenone and 1.25 gm. (0.033 mole) of sodium borohydride, 11.2 gm. (83.6%) of a colorless liquid, p-methylphenyl- α -ethanol, b.p. 95-99° at 8 mm. (lit.¹⁰³ b.p. 109-110° at 19 mm.), n_D^{28} 1.5179, was obtained after a vacuum distillation of the residue.

f. Rate Study

In a 200-ml. round-bottom flask was placed 14.1 gm. (0.117 mole) of acetophenone and 15.7 gm. (0.117 mole) of p-methylacetophenone dissolved in 100 ml. of ether, which was protected by a calcium chloride drying tube. To this was added 0.975 gm. (0.00586 mole) of selenium oxychloride. The reaction mixture was occasionally swirled and allowed to stand at room temperature for two hours. The desired precipitate was filtered, washed with fresh solvent, and dried. There was recovered 1.6 gm. of a white selenium adduct. This was reduced with excess sodium borohydride to α -phenyl ethanol and p-methylphenyl- α -ethanol. The V.P.C. analysis showed that the ratio of the alcohols was 1.00 to 1.36 respectively. This was run on an Aerograph instrument equipped with a silicone column.

Using the same technique, from 14.1 gm. (0.117 mole) of acetophenone, 17.6 gm. (0.117 mole) of p-methoxyacetophenone, and 0.975 gm. (0.00586 mole) of selenium oxychloride, 1.5 gm. of a white selenium adduct was obtained. Reduction with sodium borohydride led to α -phenylethanol and p-methoxyphenyl- α -ethanol in the ratio of 1.00 to 5.34 respectively.

Similarly from 10.8 gm. (0.0898 mole) of acetophenone, 17.6 gm. (0.0898 mole) of p-bromoacetophenone, and 0.731 gm. (0.0045 mole) of selenium oxychloride, 1.1 gm. of a white selenium adduct was obtained. Reduction with sodium

borohydride led to α -phenylethanol and p-bromophenyl- α -ethanol in the ratio of 1.00 to 0.78 respectively.

5. Miscellaneous

a. Acetophenone

In a 500-ml. round-bottom flask was added 11.6 gm. (0.03 mole) of dichloroselenoacetophenone in 300 ml. of absolute alcohol. The reaction mixture was refluxed until all the solid dissolved and then 3.90 gm. (0.06 mole) of powdered zinc, a 100% excess was added. Almost immediately red selenium formed and the reaction mixture was heated on a water bath at 90-100° for about an hour until most of the alcohol evaporated. The remaining liquid was extracted with 100 ml. of ether which was added to a separatory funnel containing 100 ml. of water. The upper ether layer was extracted and dried with anhydrous magnesium sulfate. After evaporation of the ether a distillation of the residue led to 2.2 gm. (30.9%) of a colorless liquid, acetophenone, b.p. 81-86° at 8 mm. (lit.⁷³ b.p. 88.5° corrected at 16 mm.), n_D^{28} 1.5281 (lit.⁵⁷ $n_D^{20.7}$ 1.5336).

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