SELENIUM DIOXIDE: PREPARATION, PROPERTIES, AND USE AS OXIDIZING AGENT

G. R. WAITKINS[1] AND C. W. CLARK[2]

Research Laboratories, Canadian Copper Refiners Limited, Montreal East, Quebec, Canada

Received February 14, 1945

CONTENTS

I. INTRODUCTION

While the reduction of selenium dioxide and selenites to selenium by various organic compounds was noted by many investigators before 1900, the specific nature of the oxidizing action of selenium dioxide on organic compounds was first indicated in 1930–1932 by Riley (194, 200). Since that time many papers have been published showing the wide application of this reaction to the preparation of new compounds either unobtainable or prepared only with difficulty by other methods from unsaturated hydrocarbons, aldehydes, ketones, heterocyclic nitrogen compounds, terpenes, sterols, fatty oils, and other natural products. This subject has been reviewed in the past by Dupont (62), Hirayama (107),

[1] Research Chemist, Canadian Copper Refiners, Ltd.

[2] Director of Research and Development, Canadian Copper Refiners, Limited.

Kratzl (129), Linstead (135), Mayor (150), Melnikov (152), Naves and Igolen (180), Sa (212), Stein (233), and Weygand (255a).

The present, more comprehensive review has been compiled to correlate and to extend the existing literature, in view of the increasing importance of this reagent.

II. Preparation of Selenium Dioxide

Unlike sulfur, selenium does not support combustion. In the laboratory (11, 98, 119) it is oxidized to selenium dioxide by means of strong oxidizing agents such as nitric acid. The usual procedure (199) is to add commercial selenium powder in small amounts to an excess of concentrated nitric acid. The initial reaction is highly exothermic, and clouds of brown fumes of nitrogen dioxide are evolved. The clear solution of selenious acid is fumed to remove excess nitric acid and then evaporated to dryness to dehydrate selenious acid to selenium dioxide. The crude selenium dioxide obtained in this manner is purified readily by sublimation at 317°C. or above to form glistening, white, monoclinic crystals.

A product of high purity also can be obtained by direct oxidation of selenium with air or oxygen, using traces of nitrogen oxides as catalysts to promote the reaction (59, 92, 161, 178). In this method air or oxygen is bubbled into concentrated nitric acid and then is swept through a glass tube over molten selenium. The selenium dioxide sublimes as it is formed and collects in the cooler end of the tube or in a receiving flask.

Crude selenium dioxide can be prepared commercially by digesting copper refinery slimes containing selenium with sulfuric acid at 400°F. (43). Treadwell and Fränkel (241) have described a process for the manufacture of pure selenium dioxide. According to this patent selenium vapor and excess air are thoroughly mixed, and the preheated gases are conducted through a heated layer of an indifferent porous material such as sand, asbestos, fire-brick, or mixtures of these bodies to effect quantitative conversion of the selenium to selenium dioxide. Selenium dioxide is manufactured currently by an undisclosed process. The commercial product analyzes over 99.9 per cent SeO_2, the remainder being water with the following impurities expressed in parts per million: copper, 0.5; iron, 2; tellurium, 1–2.

The selenium precipitated after reduction of selenium dioxide by various organic compounds can be recovered and converted to selenium dioxide for re-use in some instances with an efficiency of more than 95 per cent, thus making it possible to operate a cyclic oxidizing process economically. The precipitated selenium is collected on a filter and is washed with alcohol or other indifferent solvents. It is then converted to crystalline selenium, if not already in this form, by heat treatment for several hours above 100°C., ground to a fine powder, and rewashed with solvents to remove occluded organic impurities. Selenium containing an appreciable amount of organic impurity may oxidize with explosive violence if heated too strongly with nitric acid (7); therefore, it is preferable in some cases to burn the selenium in air or oxygen, using the methods outlined above.

III. Physical Properties

Selenium dioxide sublimes at 317°C. to form white monoclinic crystals that melt at 340°C. in a sealed tube. The compound has a density of 3.95 at 15°C. and a heat of vaporization of 21,600 cal. per mole. In the vapor state, selenium dioxide shows a greenish yellow color characteristic of selenium dioxide itself and not of free selenium vapor, as is demonstrated by the fact that the color is retained in the presence of free oxygen (262). The relation of vapor pressure to temperature for the equation SeO_2 (s) $\rightarrow$ SeO_2 (g) is as follows (102):

t, °C	20	70	94	124	210	260	311	315
p, mm	0	12.5	20.2	25.5	54	112.7	610.9	760

IV. Solubility of Selenium Dioxide and Selenious Acid

Of the dioxides of the sulfur group, selenium dioxide is by far the most soluble in water. It absorbs moisture from the air to form solid selenious acid, but even at ordinary temperatures this reaction is reversible and selenious acid effloresces on warm dry days to form selenium dioxide. The dissociation pressures determined by Ishikawa and Abe (112) for the reaction

$$H_2SeO_3 \text{ (s)} \rightarrow SeO_2 \text{ (s)} + H_2O \text{ (g)}$$

illustrate this point:

Temperature, °C	20	30	40	50	60	70
Pressure of H_2O(g), mm.	0.8	2.0	4.6	10.5	21.2	44.6

According to Julien (119), it is practically impossible to remove the last traces of water from selenium dioxide, since resublimed selenium dioxide that has been desiccated over phosphoric anhydride for a year still retains 0.045–0.088 per cent water. Selenious acid is very soluble in water, as shown by the following data (112) listing the moles of dissolved selenious acid in equilibrium with solid H_2SeO_3 between 20° and 70°C.; above 70°C. the solid phase changes to solid selenium dioxide.

Temperature, °C	20	30	40	50	60	70
Moles H_2SeO_3 per 100 g. H_2O	(20)	33.5	44.5	53.7	89.1	176.3

Selenious acid is weaker than sulfurous acid but stronger than the common weak acids such as acetic, benzoic, and carbonic. By the use of the glass electrode Hagisawa (91) estimated the dissociation constants for this dibasic acid to be $K_1 = 2.4 \times 10^{-3}$ and $K_2 = 4.8 \times 10^{-9}$ at 25°C. The molecular structure $HSe(OH)O_2$ has been assigned to selenious acid as the result of magnetic measurements (189).

Selenium dioxide has little or no solubility in organic solvents other than alcohols and related hydroxylic compounds. While it is possible in many cases to oxidize organic compounds by heating them directly with selenium dioxide or

solid selenious acid, the customary procedure is to dissolve these substances in a small amount of water and then to add acetic acid, dioxane, alcohol, or other indifferent solvents so as to form a more or less homogeneous solution with the organic compound being oxidized. Selenium dioxide also dissolves in hot 95 per cent sulfuric acid, and such solutions can be used in some instances. Concentrated phosphoric acid dissolves selenium dioxide on warming; at the same time it is a good solvent for many organic compounds and can be used in reactions in which a dehydrating but non-oxidizing medium is desirable (251). In reactions requiring a non-aqueous medium alcoholic solutions of selenium dioxide may be used advantageously.

Alcohols appear to dissolve selenium dioxide at ordinary temperatures by reacting to form alkyl acid selenites according to the equation (6, 101):

$$ROH + SeO_2 \leftrightarrows ROSeO_2H$$

although this is disputed by Prideaux and Green (190). Compounds of this type are obtained as crystalline solids from methanol and ethanol solutions of selenium dioxide by dehydration with calcium chloride in a desiccator. A stronger dehydrating agent such as sulfuric acid causes the alkyl acid selenite to revert to the alcohol and selenium dioxide. These alkyl acid selenites are decomposed easily by water to form the alcohol and selenious acid. Alkyl ammonium selenites result when alcoholic solutions of selenium dioxide are treated with anhydrous ammonia (52). Dialkyl selenite esters, $(RO)_2SeO$, are formed by the reaction of alcohols and selenium dioxide at higher temperatures (153). The lower dialkyl selenite esters are high-boiling liquids that can be distilled under reduced pressure without decomposition. These esters are soluble in the usual organic solvents and, like the alkyl acid selenites, are decomposed readily by water.

de Coninck (45) states that 100 parts of methanol dissolve 10.16 parts of selenium dioxide at 11.8°C. and that 100 parts of 93 per cent ethanol dissolve 6.67 parts of selenium dioxide at 14°C. No other quantitative measurements on the solubility of selenium dioxide in alcohols appear to have been reported in the literature. Qualitative experiments have shown (251) that selenium dioxide can be dissolved in many alcohols readily on warming, in some cases accompanied by slight to considerable reduction owing to the reducing action of impurities or because of the easy reducibility of the solvent itself. The following alcohols were tested: *n*-propyl, isopropyl, *n*-butyl, isobutyl, tertiary butyl, isoamyl, tertiary amyl, *n*-hexyl, methylamyl, capryl, *n*-octyl, 2-ethylhexyl, nonyl, decyl, undecyl, dodecyl, cetyl, oleyl, stearyl, benzyl, tetrahydrofurfuryl, cyclohexyl, 2-nitro-1-butyl, diacetone alcohol, ethylene glycol, glycerol, several amino alcohols, and various Cellosolve and Carbitol solvents.

V. Chemical Properties

A. Reactions with common cations

Both normal and alkali acid selenites can be prepared readily by neutralizing selenious acid with the calculated quantity of alkali hydroxide or carbonate. These colorless crystalline compounds are moderately soluble. The alkali

selenites can be heated to red heat and above without decomposition. Unlike the alkali sulfites, these compounds do not react with free sulfur, selenium, polysulfides, or polyselenides to form addition products corresponding to thiosulfates and selenosulfates.

The alkaline earth selenites are precipitated as finely divided, white powders of high refractive index when appropriate solutions are mixed at the neutral point. These compounds dissolve easily in strong acids. Like the alkali selenites they are stable to heat at high temperatures.

Elements forming tetravalent cations precipitate highly insoluble selenites from strongly acid solutions; among these are tin, titanium, cerium, zirconium, thorium, and lead. Ceric selenite is bright yellow in color, while the remaining selenites of this group are colorless. Other elements that form insoluble selenites in acid solutions are iron (Fe^{+++}), lead (Pb^{++}), mercury (Hg_2^{++}), and silver (Ag^{+}). Under certain conditions freshly precipitated metal hydroxides, such as ferric hydroxide and chromic hydroxide, quantitatively remove selenite from solution by forming insoluble adsorption compounds (181, 238). One method for the separation of selenite from copper solutions is based on this reaction with ferric hydroxide. Complex selenito-molybdates and -vanadates also can be precipitated from acid solutions containing certain heavy metal ions. The selenites of copper, nickel, zinc, and cadmium separate from weakly acid or neutral solutions. In general, the heavy metal selenites are much less stable to heat in comparison to the alkali and alkaline earth selenites. At comparatively low temperatures they decompose to yield the metal oxide and selenium dioxide or in certain cases metal oxide and selenide, free selenium, and oxygen.

B. INORGANIC OXIDIZING AND REDUCING AGENTS

While nitric acid oxidizes selenium to selenite, further oxidation to selenate appears to be impossible with this reagent or with nitric oxide at 315°C., according to Barnes (13). Stronger oxidizing agents such as fluorine, ozone, peroxide, chromate, dichromate, permanganate, chlorate, and perchlorate, however, can oxidize selenium or selenite to the hexavalent state. Selenite also is partly oxidized to selenate and in part reduced to selenium and hydrogen selenide by electrolysis. Chlorine and bromine oxidize selenium only to the tetravalent state, while iodine has little effect.

Selenium dioxide and selenites are easily reduced to free selenium by inorganic reducing agents, and many methods for the qualitative and quantitative analysis of selenium or selenite are based on such reactions. Iodide, sulfide, sulfite, bisulfite, thiosulfate, hypophosphite (120), stannous compounds, ferrous salts, hydrazine, and hydroxylamine are some of the reducing agents used for this purpose. Schott, Swift, and Yost (219) have shown the reaction of selenite with iodide to be reversible, and equilibrium measurements at 25°C. enabled them to calculate the free energies of un-ionized and ionized selenious acid.

Selenious acid is reduced to free selenium and in many cases to selenide by the action of nascent hydrogen. All metals, with the exception of gold and the platinum metals, reduce selenious acid apparently in this manner when immersed in the acid. In the presence of hydrochloric acid and selenious acid, silver

becomes covered with a film of silver selenide, this reaction being sensitive to one part of selenium in 50,000 parts of solution.

Gaseous substances such as hydrogen, ammonia, and phosphine reduce selenium dioxide with the emission of light and heat to form selenium and, under certain conditions, hydrogen selenide. Carbon reduces selenium dioxide to selenium, according to Berzelius. Carbon monoxide, however, does not appear to react even when activated by sunlight or ultraviolet light, and Barnes (14) found it possible to sublime selenium dioxide unchanged with carbon monoxide in a quartz tube. Sulfur, phosphorus, arsenic, boron, and silicon reduce the dioxide on heating. Dry sulfur dioxide is said to have no effect on selenium dioxide.

While selenic acid contains more oxygen than selenious acid, many of the reducing agents that react rapidly with selenite reduce selenate to selenium at a much slower rate. Selenic and selenious acids appear to be comparable to perchloric and chloric acids in this respect. On the other hand, in some instances selenic acid shows oxidizing properties comparable to the peroxides, since it is quantitatively reduced to selenious acid on boiling with hydrochloric or hydrobromic acids, chlorine and bromine being evolved in this reaction. Selenates also can be reduced to selenite by treatment with ferrous salts in acid solutions (250).

In an earlier review relating to the industrial uses of selenium and tellurium (252), it was pointed out that selenium dioxide and selenic acid are less stable than corresponding sulfur and tellurium compounds, as shown by the following heats of formation expressed in kilogram-calories:

	kg.-cal.		*kg.-cal.*
SO_2 (l)	75.27	H_2SO_4 (l)	189.75
SeO_2 (s)	57.08	H_2SeO_4 (l)	126.6
TeO_2 (s)	78.3	H_2TeO_4 (aq.)	169.5

The following similar figures are quoted from Yost and Russell (263):

	HEAT OF FORMATION	FREE ENERGY OF FORMATION	STANDARD ENTROPY S^0_{298}
	18° *calories*	*calories*	*calories per degree*
SO_2	70,920	−69,660	59.4 (gas)
SeO_2	56,360		62.5 (gas)
TeO_2	77,580	−64,320	17.4 (solid)

MOLAL FREE ENERGIES OF FORMATION F^0_{298}	
	calories per mole
SO_2 (g)	−71,735
SeO_2	
H_2SO_3	−128,535
H_2SeO_3	−101,361
SO_3^{--}	−116,400
SeO_3^{--}	−87,890

This marked difference in the heats and free energies of formation may explain why selenium dioxide, selenites, and selenates have outstanding oxidizing properties in comparison to their tellurium and sulfur analogues; that is, oxygenated selenium compounds are able to give up their oxygen more readily to reducing agents. Fisher and Eisner (77) find that tellurium dioxide, for example, is far less satisfactory than selenium dioxide as an oxidant for organic compounds.

A clearer expression of the oxidizing power of selenites and selenates is afforded by comparing the potential values relating to the important oxidation states of sulfur, selenium, and tellurium and their compounds in acid solution. The equations given below are taken from *Oxidation Potentials* by Latimer (132).

Zerovalent to tetravalent state (acid solution)

$$3H_2O + S = H_2SO_3 + 4H^+ + 4e^- \qquad E^0 = -0.45 \text{ v.}$$
$$3H_2O + Se = H_2SeO_3 + 4H^+ + 4e^- \qquad E^0 = -0.74 \text{ v.}$$
$$2H_2O + Te = TeO_2\ (s) + 4H^+ + 4e^- \qquad E^0 = -0.529 \text{ v.}$$
$$2H_2O + Te = TeOOH^+ + 3H^+ + 4e^- \qquad E^0 = -0.559 \text{ v.}$$

Tetravalent to hexavalent state (acid solution)

$$H_2O + H_2SO_3 = SO_4^{--} + 4H^+ + 2e^- \qquad E^0 = -0.20 \text{ v.}$$
$$H_2O + H_2SeO_3 = SeO_4^{--} + 4H^+ + 2e^- \qquad E^0 = -1.15 \text{ v.}$$
$$4H_2O + TeO_2 = H_6TeO_6\ (s) + 2H^+ + 2e^- \qquad E^0 = -1.02 \text{ v.}$$

It may be of interest to note that Carter, Butler, and James (39) observed that selenium, although insoluble in hydrochloric acid, dissolves in concentrated hydrochloric acid in the presence of selenium dioxide. These authors measured the oxidation potential of the system selenium–selenium dioxide–concentrated hydrochloric acid and the effect of changes in concentration of selenium and selenium dioxide and found E (20°C.) to be -0.572 volt.

VI. Oxidation of Organic Compounds

A. Mechanism of the Reaction

Selenium dioxide functions as a mild oxidizing agent over a wide temperature range, and oxidations of organic compounds with this substance have been likened to autoöxidation or peroxidation (64, 69). At ordinary temperatures, specific oxidation takes place as follows: in compounds containing methylene or methyl groups activated by an adjacent double bond, carbonyl, or aldehyde group, or adjacent benzene nucleus, the activated group is oxidized to the corresponding ketone or aldehyde group. Adjacent nitrogen atoms in heterocyclic compounds also activate the oxidation of the methylene or methyl group. Some of these oxidations can be carried out at room temperature with the aid of sunlight or ultraviolet light. Yields and the types of oxidation products obtained are affected by the solvent used. In glacial acetic acid, acetic anhydride, and sometimes in alcohol solvents the reaction generally proceeds only as far as the alcohol stage. Many instances have been described in which selenium dioxide acts chiefly as a mild dehydrogenating agent; however, it is rarely that this oxidant splits the C—C chain in the way that lead tetraacetate does.

Even at temperatures of 350–400°C. and above, where the specific oxidizing action of selenium dioxide is less pronounced, this oxidant exhibits unique characteristics. Emeleus and Riley (64) have observed that photographs of the flame spectra obtained by burning ammonia and diverse organic compounds in selenium dioxide vapor are identical in the visible region and show no lines in the ultraviolet spectrum. Inasmuch as selenium burning in oxygen alone gives an identical spectrum, and the water bands are not excited as is usually the case with burning hydrocarbons, their results prove definitely that the chief emission from the flames of compounds burning in selenium dioxide vapor is characteristic of selenium and perhaps of its oxide but not of the substance undergoing oxidation. These authors conclude that the selenium dioxide molecule possibly forms a definite intermediate compound with the substance undergoing oxidation (analogous to peroxidation) and the selenium is eliminated at a relatively low temperature, leaving intermediate oxidation products that undergo a non-luminous thermal decomposition, while radiation from the selenium molecule occurs readily and the decomposition of the intermediate yields enough energy to excite the selenium vibrations. In a study of the mechanism by which alcohols are oxidized with selenium dioxide, Melnikov and Rokitskaya (153) have shown that the lower alcohols react with the dioxide to form dialkyl selenite esters and that these intermediate products, when heated to 300°C. in a nitrogen stream, decompose to form the corresponding aldehyde, selenium, and water. Intermediate oxidation products containing selenium also have been isolated in many other reactions carried out at ordinary temperatures; therefore, this view of the mechanism of the oxidation appears to be well established.

In the type of oxidations discussed up to this point, selenium dioxide undergoes reduction to free selenium and the reaction stops when the dioxide has been completely utilized in this manner. Most of the precipitated selenium is recoverable and can be reoxidized to selenium dioxide for further use. In hot concentrated sulfuric acid, however, it is possible for selenium and selenium dioxide to function as catalytic agents.[3] The oxidizing action of selenium dioxide in sulfuric acid has long been known, and a test for the identification of alkaloids by their color reactions with this reagent has often been used in the past. Selenium, alone or in conjunction with mercury, has been found to act as a powerful catalyst in the Kjeldahl method for the analysis of nitrogen using concentrated sulfuric acid (29, 133, 165). The catalytic action of selenium in the concentrated sulfuric acid solution is thought to be caused by its ability to function as a reversible oxidizing and reducing agent in the manner shown by the following equations, according to Sreenivasan and Sadisivan (229):

[3] R. E. Schmidt (Bull. soc. ind. Mulhouse **84**, 430 (1914); see J. Houben, *Das Anthracen und die Anthraquinone*, p. 323, Georg Thieme, Leipzig (1929)) discovered that the oxidation of anthraquinone and its derivatives by fuming sulfuric acid with the introduction of phenolic groups (Bohn-Schmidt reaction) is catalyzed by traces of selenium or mercury. It was thought that selenium acted as a catalyst, possibly in the following manner:

$$SeO_2 = Se + O_2$$
$$Se + 2SO_3 = SeO_2 + 2SO_2$$

(1) $Se \leftrightarrows SeO_2 \leftrightarrows SeO_3$
(2) $Se \leftrightarrows SeO_2$ (mercury absent)
(3) $SeO_2 \leftrightarrows SeO_3$ (mercury present)

In the presence of mercury the reversible system (equation 1) predominates; in the absence of mercury, equation 2 represents the probable reaction. In either case selenium acts as a carrier for oxygen, and the oxygen is rendered active for the rapid oxidation of organic matter. As the result of a comprehensive study of reactions in concentrated sulfuric acid, Milbauer (166–168) and Milbauer and Mikolasek (169) similarly conclude that selenium functions as a catalyst in this medium. These authors show that selenium dissolves unchanged in concentrated sulfuric acid below 200°C. to give a grass-green solution. Oxidation of selenium to selenium dioxide proceeds slowly at approximately 200°C. and is complete at 300°C.

$$Se + 2H_2SO_4 \rightarrow SeO_2 + 2SO_2 + 2H_2O$$

Mercury appears to catalyze this oxidation of selenium by sulfuric acid and in addition undergoes further reaction as follows:

$$SeO_2 + 2HgSO_4 \rightarrow Hg_2SO_4 + SeO_3 + SO_3$$

B. ORGANIC OXIDATIONS BY TYPES

1. Saturated compounds

Saturated hydrocarbons, alcohols, ethers, acids, esters, and most halogenated compounds are not attacked by selenium dioxide at low temperatures; however, oxidation may occur at higher temperatures.

In discussing the solubility of selenium dioxide in alcohols, it was indicated that the lower alcohols dissolve the dioxide at ordinary temperatures by forming alkyl acid selenites and that the selenium dioxide is recovered unchanged on evaporating the alcohol. Dialkyl selenite esters result at higher temperatures and the methyl, ethyl, propyl, butyl, and isobutyl esters have been prepared in this manner by Melnikov and Rokitskaya (153). These esters decompose to form the corresponding aldehyde, selenium, and water upon heating at 300°C. in a nitrogen atmosphere, while further oxidation of the aldehyde produces carbon dioxide in most cases. Emeleus and Riley (64) observe that ethyl ether and methyl, ethyl, and propyl alcohols burn completely with a characteristic moonlight-like flame in selenium dioxide vapor at about 400°C. and state that intermediate oxidation products are formed when the oxidation occurs at lower temperatures. Astin, Newman, and Riley (7) report that glyoxal is obtained in 5 per cent yield when ethanol is reacted at 230°C., while *n*-propyl and *n*-butyl alcohols give complex products, including some alkyl selenite.

On the other hand, certain alicyclic saturated alcohols are reactive at comparatively low temperatures. Menthol, for example, is oxidized and dehydrogenated on refluxing with selenium dioxide and ethanol to form hydroxythymoquinone, thymol, and menthane (106), while borneol and isoborneol give camphorquinone in 60 per cent yield (3, 106).

Lead tetraacetate oxidizes glycols and other polyhydroxy compounds at comparatively low temperatures by splitting the —CHOH—CHOH— linkage, but selenium dioxide does not appear to react except possibly to form addition products analogous to the alkyl acid selenites. Astin and Riley (8) were able, however, to oxidize methyl tartrate and ethyl tartrate with selenium dioxide and to obtain small amounts of methyl fumarate and ethyl ketohydroxysuccinate, respectively. This would seem to indicate that this reagent shows a mild dehydroxylating or oxidizing action with certain types of polyhydroxy compounds.

The following observations are of interest with respect to the oxidation of other types of saturated compounds: Glyoxal, acetic acid, and carbon dioxide are formed when ethane reacts with selenium dioxide vapor at 350–400°C. (198). While formic and acetic acids can be refluxed unchanged with selenium dioxide, propionic acid is oxidized to pyruvic acid in 2 per cent yield under comparable conditions (54). Acetic anhydride is satisfactory as a solvent for carrying out other oxidations, but under prolonged refluxing alone with selenium dioxide it yields 17 per cent of glyoxylic acid (187). Saturated fatty acids, such as lauric, myristic, palmitic, and stearic, are dehydrogenated to undecene, tridecylene, pentadecene, and heptadecene, respectively, on heating at 300°C. with selenium dioxide in sealed tubes, according to Yokoyama (261). Ethyl acetoacetate is oxidized at 90°C. in small yield to ethyl α,β-diketobutyrate (177); diethyl malonate yields 32 per cent of ethyl mesoxalate (7, 194, 196) and some diethyl dihydroxymalonate at 130°C. (177); diethyl succinate is dehydrogenated at 170°C. to ethyl hydrogen fumarate and fumaric acid (7); while ethyl malate yields ethyl diketosuccinate and degradation products under certain conditions (6).

2. Unsaturated compounds

Selenium dioxide readily oxidizes methylene or methyl groups adjacent to the double bond in many unsaturated aliphatic, alicyclic, and polycyclic compounds such as the terpene hydrocarbons. Ordinarily, a ketone or aldehyde results, but oxidation may be stopped at the alcohol stage by using glacial acetic acid or acetic anhydride as solvent. The oxidation product then is usually isolated as the acetate. In all cases the double bond is preserved when the reaction is carried out at ordinary temperatures. Compounds containing a triple bond are attacked adjacent to this bond, although a few cases are known in which selenium dioxide adds oxygen directly at the bond.

Methylene and methyl groups adjacent to a benzene nucleus also are activated and are oxidized to ketones and aldehydes or carboxylic acids. Benzene itself does not react with selenium dioxide except at high temperatures in the vapor phase; however, polycyclic aromatics such as naphthalene, anthracene, phenanthrene, etc., are attacked to varying extent at lower temperatures.

(*a*) *Unsaturated aliphatic compounds:* In the gaseous state at 220–240°C., ethylene reacts with selenium dioxide to produce glyoxal in yields of more than 80 per cent (138, 195, 197, 198), while methylglyoxal is formed in 19 per cent yield from propylene (198) indicating, therefore, that selenium dioxide shows a

tendency to saturate the double bond at high temperatures. Dreyfus also claims the use of selenium dioxide along with other catalysts for converting olefins to glycols and oxides (58).

At lower temperatures, in the presence of a solvent, all unsaturated aliphatic hydrocarbons appear to react at positions adjacent to the double bond. A comprehensive study of many types of these hydrocarbons has been made by Guillemonat (89).

Pulverized selenium dioxide is introduced slowly into a mixture of acetic acid, acetic anhydride, and excess hydrocarbon with continuous stirring to prevent the dioxide from settling to the bottom of the reaction flask. The mixture is refluxed for 10 hr., excess acetic acid and acetic anhydride are removed by washing with water, and the crude acetate is steam distilled. Saponification of the acetate with barium hydroxide yields the alcohol oxidation product. Various solvents can be used, including pyridine, ethanol, xylene, and water, but acetic acid appears to be most favorable both as to yield and as to quality of product. Hydrocarbons having completely substituted ethylenic carbon atoms are only partly oxidized and the oxidation occurs on the carbon atom in the alpha position to the substituted carbon: thus, for example, $RCH_2C(CH_3)=CCH_3$ is oxidized to $RCHOHC(CH_3)=CCH_3$. The rates of oxidation are so different that only one of the possible alcohols forms if the radicals in the alpha position are different; in order of decreasing ease of oxidation the radicals are CH_2, CH_3, and CH. Hydrocarbons having neither ethylenic carbon atom completely substituted also are oxidized in the alpha position to the ethylenic carbon. The CH_2 radical again is oxidized more readily than CH_3, and if present on each side of the ethylenic carbon atoms both CH_2 groups are oxidized to form a mixture of alcohols. A double bond at the end of a chain is as active as a bi-secondary bond but, owing to transposition, a primary alcohol forms instead of a secondary alcohol; for example, 1-hexene yields 2-hexen-1-ol.

To explain some of these reactions, Guillemonat suggests the following equations, in which R is a radical having an ethylenic bond:

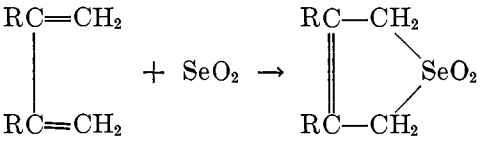
(1) $4RCH_2H + SeO_2 \rightarrow (RCH_2)_4Se + 2H_2O$
(2) $(RCH_2)_4Se + H_2O \rightarrow (RCH_2)_2Se + RCH_3 + RCH_2OH$
(3) $(RCH_2)_2Se + H_2O \rightarrow RCH_2OH + RCH_3 + Se$

Equations 2 and 3 show that a portion of the original hydrocarbon is recovered unchanged even when the theoretical amount of selenium dioxide is used. The formation of an alkyl acetate also is explained, since acetic acid may supplant water in the same equations.

Selenium dioxide also appears to oxidize the carbon atom adjacent to the double bond in unsaturated compounds of greater complexity. Practical application of this fact has been suggested by Turk, Dawson, and Soloway (245), who propose a method for the synthesis of conjugated fatty oils by the oxidation of olive, linseed, cottonseed, castor, and other unsaturated oils with selenium dioxide in an alcoholic medium and subsequent dehydration of the hydroxylated product to form a conjugated material. Linseed oil treated in this

manner with only enough selenium dioxide to hydroxylate one fatty acid chain of the linseed oil molecule yields a final product showing a diene value of 24.8 and indicating 86 per cent conjugation of the one fatty acid chain. The same procedure with cottonseed oil gives a final product having a diene number of 17.9 and indicating about 62 per cent conjugation.

Backer and Strating (9) show that substituted butadiene derivatives, but not butadiene itself, react with selenious acid in chloroform solution at room temperature to form cyclic selenones:



These products are not very stable and are decomposed readily by moisture on standing. However, in a study of polyene synthesis from certain hydrocarbons having two non-conjugated ethylenic bonds in the same molecule, J. Schmitt (218) has made the important observation that selenium dioxide acts as a selective dehydrogenating agent at fairly low temperatures and makes possible the preparation of compounds containing a conjugated series of double bonds. Tetraphenylhexatriene is obtained from 1,1,6,6-tetraphenyl-1,5-hexadiene by refluxing with acetic acid and selenium dioxide, while 1,6-dibiphenylenehexatriene is prepared in the same way from 1,6-dibiphenylene-1,5-hexadiene.

The few acetylenic hydrocarbons that have been studied appear to react with selenium dioxide in about the same manner as corresponding ethylenic hydrocarbons. Truchet (242) prepared 3-hydroxy-1-heptyne in 27 per cent yield by reacting 1-heptyne and selenium dioxide in ethanol, while 3-hydroxy-1-octyne was obtained from 1-octyne. On the other hand, Truchet (243) showed that methylphenylacetylene appeared to add selenium dioxide and give a product that was hydrated in alkaline solution to ethyl phenyl ketone.

(*b*) *Unsaturated alicyclic compounds:* Guillemonat (89) observed that in unsaturated alicyclic hydrocarbons with substituted ethylenic carbon atoms, oxidation in acetic acid plus acetic anhydride solution occurs in the alpha position to the most substituted carbon atom and also in the cycle if it is possible. Oxidation of the CH group leads to conjugated dienes as the result of dehydration of the tertiary alcohol formed, and conjugated dienes may also result from the oxidation of hydrocarbons having cyclic bi-tertiary double bonds. For example, 1-ethylcyclohexene yields the acetate of 1-ethylcyclohexen-6-ol; 1,6-dimethylcyclohexene is oxidized to five fractions, each fraction containing *o*-xylene and 2,3-dimethyl-1,3-cyclohexadiene with an undetermined liquid; while 1,2-dimethylcyclohexene yields one fraction consisting of *o*-xylene and 2,3-dimethyl-1,3-cyclohexadiene and a second fraction containing a mixture of one ethylenic acetate and one dienic acetate.

While not so reactive as compounds having double-linked tertiary carbon atoms, alicyclic hydrocarbons with bi-secondary ethylenic bonds give yields as high as 30–40 per cent. The alpha position is attacked and the CH_2 group is

more reactive than CH, with both alpha CH_2 groups being oxidized simultaneously. Transpositions of the allylpropenylic type occur readily in certain cases. Thus, cyclohexene yields the acetate of 1-cyclohexen-3-ol; 3-methylcyclohexene gives 6-methylcyclohexanol and small amounts of toluene, 4-methylcyclohexene, and 4-methylcyclohexen-3-ol; and 4-methylcyclohexene forms a mixture of the acetates of 4-, 5-, and 6-methylcyclohexen-3-ols, with the first predominating. In conjunction with the three equations proposed by Guillemonat to explain the mechanism by which unsaturated aliphatic compounds are oxidized, the following equation is proposed by him to explain the formation of dienes having conjugated systems:

$$(CH_3CH{=}C(CH_3)CH_2)_2Se \rightarrow CH_2{=}CHC(CH_3){=}CH_2 + (CH_3)_2C{=}CHCH_3 + Se$$

In the presence of selenium dioxide cyclohexene is oxidized by hydrogen peroxide to *trans*-cyclohexanediol in 45 per cent yield; 1,2-diols also result on oxidizing cyclopentadiene and piperylene under the same conditions (225).

Monocyclic terpene hydrocarbons are oxidized by selenium dioxide in much the same manner as the simpler unsaturated alicyclic compounds with the carbon atom adjacent to the double bond being attacked. Δ^1-Menthene gives carvotanacetone, while Δ^3-menthene yields Δ^3-menthen-5-one, according to Borgwardt and Schwenk (25, 223, 224). α-Phellandrene, with two double bonds in the ring, reacts to give cuminaldehyde and *p*-cymene, both materials being dehydrogenation products (25, 104).

(*c*) *Unsaturated polycarbocyclic compounds:* Bicyclic terpene hydrocarbons react quite readily with selenium dioxide at moderate temperatures. Usually, a complex mixture of products results and the yields depend on temperature, time of reaction, solvent, and the amount of selenium dioxide used. A review of the existing literature dealing with the oxidation of β-pinene is instructive from this standpoint. Dupont, Allard, and Dulou (59) obtained what they thought was pure pinocarvone in 35 per cent yield by refluxing a mixture of β-pinene, selenium dioxide, and alcohol, while Zacharewicz (265) showed that both pinocarvone and pinocarveol were formed. In a careful study of this reaction, Stallcup and Hawkins (230) treated β-pinene in molar ratio with selenium dioxide alone, and in water, alcohol, acetone, benzene, hexane, ether, carbon tetrachloride, and pyridine for approximately an average time of 10 hr. to obtain 15–34 per cent of a steam-volatile product that was shown to contain mostly carvopinone with some pinocarvone. Joshel and Palkin (117), however, demonstrated that pinocarveol was obtained as the main product in 42 per cent yield by the reaction of β-pinene in ethanol with slightly less than 0.5 mole of selenium dioxide per mole of β-pinene. Finally, Stallcup and Hawkins (231) showed that in acetic acid or acetic anhydride the products were largely pinocarvyl acetate with some pinocarveol, carvopinone, and pinocarvone. All of these investigators observed the fact that much of the selenium remained in the non-volatile reaction products in the form of complex, organic selenium compounds. In the case of the reaction of camphene with selenium dioxide, Zacharewicz (264) obtained camphene selenide as the sole product.

The effect of temperature on the type of product obtained is well illustrated by the work of Campbell and Harris (37), who oxidized $\Delta^{9,10}$-octalin with selenium dioxide in acetic anhydride: $\Delta^{9,10}$-octalol-1 acetate was obtained at 5°C., $\Delta^{9,10}$-octalindiol-1,5 diacetate at 30°C., and a hexahydronaphthalenediol-1,5 diacetate was isolated as the main product upon carrying out the reaction at 120°C.

(*d*) *Aromatic compounds:* Selenium dioxide attacks methyl or methylene groups attached to a benzene nucleus, but these reactions generally require high temperatures and give low yields of oxidation products. Many aromatic derivatives, however, are attacked vigorously at low temperatures to form resinous products of unknown constitution. Among these are phenols, cresols, aminophenols, phenol ethers, and amines. Amine reactions are discussed more fully in the section on nitrogen compounds, and it is shown further on that definite organic selenium compounds can be isolated by reacting phenolic compounds with selenium dioxide in concentrated sulfuric acid.

Toluene is oxidized by selenium dioxide to benzoic acid in only 27 per cent yield at 300°C. in a sealed tube (54). Dinitro- and trinitro-toluenes are unaffected on refluxing with selenium dioxide in alcohol (76). At 300°C. dibenzyl reacts to produce both stilbene and benzil; in this reaction stilbene is formed first by dehydrogenation and then is oxidized to benzil, according to Deupree and Lyons (54). Stilbene itself yields 86 per cent benzil at 260–280°C. (6) and tolane gives a 35 per cent yield of benzil at 280°C. (187). Diphenylmethane appears to undergo oxidation more readily than triphenylmethane (76). Compounds containing partly substituted methyl groups adjacent to the benzene nucleus are more reactive. For example, at reflux temperatures benzyl alcohol is converted completely to benzaldehyde, while benzyl chloride and *p*-nitrobenzyl chloride lose chlorine and give the corresponding aromatic aldehydes in about 50 per cent yield (76).

Polycyclic aromatic hydrocarbons differ greatly in their ease of reaction with selenium dioxide. Anthraquinone is obtained in about 75 per cent yield by treating anthracene in nitrobenzene (6) or molten anthracene and selenium dioxide without solvent (187). Phenanthrene (6, 187) and fluorene (187), however, produce only about 5 per cent yields of phenanthraquinone and fluorenone, respectively. On the other hand, Badger (10) states that 1,2,5,6-dibenzfluorene gives a satisfactory yield of 1,2,5,6-dibenzfluorenone. Acenaphthene and selenium dioxide in acetic acid at 150–200°C. yield a mixture of acenaphthylene glycol, acenaphthylene, polyacenaphthylene, and dinaphthylenecyclobutane; oxidation by lead tetraacetate yields only the last three products (173).

Although methyl groups attached to a polycyclic nucleus require a fairly high temperature for reaction, selenium dioxide has a definite use in this type of oxidation, since strong oxidizing agents such as chromic acid or permanganate often produce resinous products entirely. With selenious acid in an autoclave at 230–240°C., Kacer (121–123) claims that 2-methyl- and 6-methyl-benzan-

threnes are oxidized to the corresponding benzanthrenealdehydes, 5-methylnaphthanthraquinone forms a carboxylic acid, and 2-benzylbenzanthrone produces 2-benzoylbenzanthrone. Copp and Simonsen (50) report that 9- and 10-methylmesobenzanthrones are oxidized to the corresponding mesobenzanthronealdehydes in approximately 25 per cent yield. Similarly, with selenium dioxide in nitrobenzene, 2-methyl-1,1′-dinaphthyl ketone produces 2-carboxy-1,1′-dinaphthyl ketone, whereas permanganate oxidation does not give any useful products (49).

(*e*) *Complex unsaturated compounds:* Much work has been done in the recent past on the structure and synthesis of naturally occurring sterols, bile acids, sex hormones, sapogenins, polyterpenes, and other complex compounds. As would be expected, selenium dioxide, among other reagents, has been used in these studies as an aid in elucidating the structure of certain products and for the preparation of new derivatives. Specific compounds oxidized and the products obtained are listed in table 3 at the end of this review.

In their work on sterols and bile acids Callow and Rosenheim (35) showed that selenium dioxide acted mainly as a dehydrogenating agent upon reacting with ergosterol, α-ergostenol, and apocholic acid, whereas oxide formation was the characteristic reaction with cholesterol and dihydroergosterol. Cholestenediols were obtained, however, by reacting cholesterol with selenium dioxide in alcohol, acetic acid, or nitrobenzene, as shown by Butenandt and Hausmann (33) and by Rosenheim and Starling (202). Montignie (175) proposed the use of selenious acid to differentiate ergosterol from other sterols, since ergosterol reacted with this reagent in 2 min. at 95°C., while cholesterol, phytosterol, and stigmasterol gave negative tests. Other references to work in this field are as follows: oxidation of cholesterol to cholestanone at 230°C. using elemental selenium (56); the treatment of cholesterol derivatives (63), lanosterol derivatives (19), clionastrol (21), sitosterol and stigmasterol derivatives (145, 146); the reaction of apocholic and norcholanic acid derivatives (34, 210); and the synthesis of substances related to the sterols (148).

The use of selenium dioxide for the preparation of sex hormone derivatives related to pregnenolone and androsterone has been reported by Marker, Crooks, and Wittbecker (144), Ruzicka and Plattner (209), and in several patents (164, 227, 228). Howeg and Herloff (108) claim in a patent that both selenium dioxide and lead tetraacetate break the cyclopentane ring in estradiol; if so, this is the first case to be reported of ring rupture by the use of selenium dioxide at ordinary temperatures.

Studies relating to the oxidation of complex polyterpene compounds with selenium dioxide have been made by Bilhani, Kon, and Ross (22), Jones and Meakins (116), Mowrer, Green, and Spring (176), Picard and Spring (185), and Ruzicka and his collaborators (204–208, 211). Sapogenin derivatives have been studied by Marker (143) and by Marker and Turner (147). Osajetin and pomiferitin compounds derived from osage orange pigments have been reacted with selenium dioxide by Wolfram and Mahan (258).

3. Oxidation of aldehydes and ketones

The discovery made by Riley (194) that selenium dioxide exerts a specific oxidizing action on methyl and methylene radicals adjacent to the carbonyl group in aldehydes and ketones has been widely applied to the preparation of many previously inaccessible glyoxal, α,β-diketone, and triketone derivatives from aliphatic, alicyclic, aromatic, and terpene aldehydes and ketones. The rather good yields obtained in these reactions are remarkable because of the ease with which the oxidation products polymerize under normal conditions.

Riley, Morley, and Friend (200) obtained methylglyoxal in 60 per cent yield from acetone and almost a 100 per cent yield of glyoxal from acetaldehyde. They found in general that the higher ketones and aldehydes were less reactive than the first members of each series. Methyl groups appeared to be more reactive than methylene, as shown by the fact that ethyl methyl ketone produced mainly ethylglyoxal rather than biacetyl. Likewise, a comparison of the reactivity of acetophenone and phenylacetaldehyde led to the same conclusion, since these compounds gave phenylglyoxal in yields of 50 and 35 per cent.

The mechanism by which aldehydes and ketones are oxidized with selenium dioxide has been studied in detail by Melnikov and Rokitskaya (154, 156–160). These authors state (154) that carbonyl compounds are oxidized chiefly to aldehydo ketones and α,β-diketones with organic selenium compounds, products of deeper oxidation being formed in smaller amounts. Acetone and butyraldehyde react rapidly, whereas triacetonemannitol and the acetal of butyraldehyde oxidize only after some hydrolysis has occurred, thus making it apparent that carbonyl compounds react only through their enol forms. Selenious acid adds to produce enol esters (analogous to the reaction of alcohols with selenium dioxide), and these decompose in the manner suggested by Melnikov and Rokitskaya (153) and previously discussed in the section dealing with the oxidation of saturated compounds. The reactions of acetone, ethyl methyl ketone, methyl *n*-propyl ketone, and cyclohexanone with selenium dioxide are bimolecular. Since selenious acid reacts with amylene and cyclohexene by adding to the double bond, with the addition compound decomposing to give organic selenium compounds, aldehydes, alcohols, and hydrocarbons of higher molecular weight, it is inferred that products of deeper oxidation of carbonyl compounds probably result from similar addition of selenious acid to the double bond of the enol form.

The kinetics of ketone oxidation by selenium dioxide were studied (156), with additional experimental evidence given to show that these oxidations are bimolecular reactions. Equivalent amounts of ketone and selenious acid in 75 per cent acetic acid were reacted at 20° and 50°C. for 1 to 6 hr. The selenium precipitated during the course of each reaction was collected, washed with water and ether, and dried to constant weight at 100°C. The comparative graphs, obtained by plotting selenium recovered *versus* time, for a series of symmetrical alkyl ketones and for a series including unsymmetrical alkyl ketones, acetophenone, and pinacolone, indicate that the rate of oxidation (enolization) decreases gradually with increasing molecular weight. This is shown also by

alkyl aryl ketones in the series from methyl phenyl ketone to ethyl phenyl ketone and phenyl *n*-propyl ketone. Alicyclic ketones are more rapidly oxidized than aliphatic ketones, which in turn are more easily oxidized than aromatic ketones. The gradual decrease in the oxidation rate of methyl propyl ketone, isopropyl methyl ketone, and pinacolone shows the influence of primary, secondary, and tertiary radicals on the degree of enolization. Oxidation of isomeric amyl methyl and hexyl methyl ketones (160) shows that the oxidation velocity depends greatly on structure. Ketones containing an even number of CH_2 groups between the carbonyl group and a secondary radical are less easily enolized than normal ketones or those ketones containing an odd number of CH_2 groups between the carbonyl group and a secondary radical. Ketones having a secondary or tertiary group attached to carbonyl are still less easily enolized. At 30°C. in 75 per cent acetic acid the order of increasing oxidation rate for a series of substituted acetophenones (159) is *m*-$NO_2C_6H_4COCH_3$, *p*-$BrC_6H_4COCH_3$, *p*-$ClC_6H_4COCH_3$, $C_6H_5COCH_3$, *p*-$CH_3OC_6H_4COCH_3$, *p*-$CH_3C_6H_4COCH_3$, *p*-$IC_6H_4COCH_3$, and $C_6H_5CH_2COCH_3$.

A study of the oxidation of acetone, ethyl methyl ketone, and methyl propyl ketone in absolute and aqueous methanol, ethanol, butanol, isobutyl alcohol, and isoamyl alcohol indicates that the relation of rate constants to the structure of the ketones is the same as for their reaction in 75 per cent acetic acid (158). The constants are lower in the anhydrous alcohols than in the acetic acid, owing to the formation of complexes between the alcohols and the ketones. The addition of water decomposes these complexes and thereby increases the rate of oxidation. The reaction rate increases with the molecular weight of the normal alcohols and is highest in isobutyl alcohol solution.

Oxidation, with selenious acid in 95 per cent acetic acid, of a series of aliphatic aldehydes (157) having normal and branched chains shows that the oxidation velocity decreases with increasing molecular weight with the exception of acetaldehyde, whose reaction constant is considerably smaller than that of propionaldehyde (explainable by the easy polymerization of acetaldehyde in acid medium). The reaction constant also is decreased in the iso compounds as compared with aldehydes having a normal chain.

The most interesting case of dehydrogenation of a ketone with selenium dioxide appears to be that reported by Armstrong and Robinson (4), who obtained diacetylethylene in 15 per cent yield from acetylacetone. This reaction appears to be comparable to the dehydrogenation of several 1,5-hexadiene derivatives to hexatrienes, as shown by Schmitt (218). Godchot and Cauquil (85) report that dehydrogenation products as well as the expected 1,2-diones are formed in the reaction of 1-methyl-2-, 1-methyl-3-, and 1-methyl-4-cyclohexanones with selenium dioxide in ethanol at 80°C. Under the same conditions cycloheptanone gives the 1,2-diene but cyclooctanone yields only 8-ethoxy-1,2-cyclooctandione. Hirayama (103, 104) finds that monocyclic terpene ketones such as menthone and piperitone are dehydrogenated in the ring to produce thymoquinone derivatives.

Camphor reacts with selenium dioxide in a normal manner, giving camphor-

quinone in 65 per cent yield (3). When the reaction is carried out in ethanol, toluene or xylene, or acetic anhydride the corresponding yields are 27, 88, and 95 per cent, according to Vene (248). Vene finds, however, that camphor derivatives exhibit rather unusual reactions, since α-bromo- and α-chlorocamphors lose halogen to form camphorquinone, while ethylcamphor yields both ethylidenecamphor and camphorquinone on heating with selenium dioxide alone. Benzylcamphor forms benzylidenecamphor in 95 per cent yield; benzylidenecamphor is remarkable in that it is unaffected by heating with selenium dioxide at 200°C. Furthermore, isonitrosocamphor is attacked by selenium dioxide in a unique fashion with scission of the ring to give fair yields of camphornitrile and camphoric anhydride.

The oxidation of a methylene group situated between two carbonyl groups to form a triketone has been accomplished in several cases. The oxidation of 1,3-diketohydrindene by selenium dioxide in dioxane solution furnishes the best method for the preparation of ninhydrin (triketohydrindene hydrate) (240a). Triketopentane is obtained in 12–25 per cent yield from acetylacetone by reaction with selenium dioxide alone or in ethanol (36, 186), and dimesityl triketone in good yield from di(β-isoduryloyl)methane (81). Nevertheless, Piutti (186) was unable to prepare a triketone from acetylbenzoylmethane, $CH_3COCH_2COC_6H_5$.

4. Oxidation of nitrogen compounds

Selenious acid, like other acids, combines with aliphatic and aromatic amines at low temperatures to form crystalline, substituted ammonium salts (6, 40, 54, 101). The direct addition of anhydrous selenium dioxide to an amine also may occur as shown in the case of piperidine, which reacts in cold benzene to produce the addition product $C_5H_{10}NH \cdot SeO_2$ (141, 142). With increasing temperature, both aliphatic and aromatic amines oxidize rapidly to yield complex resinous or tarry products. Aniline, for example, first forms aniline selenite and then more complex, dark blue to black compounds that are insoluble in water. The reaction between most amines and selenium dioxide is highly exothermic at high temperatures and usually proceeds with explosive violence. In concentrated sulfuric acid solution selenium dioxide gives characteristic color reactions and organic selenium compounds with aromatic amines and alkaloids. Aromatic *o*-diamines undergo a special reaction with selenium dioxide to form piaselenols. These compounds and the color reactions in sulfuric acid are discussed in following sections of this paper.

Heterocyclic amines having a tertiary nitrogen in the ring, such as pyridine and quinoline, may be refluxed with selenium dioxide without change. At 300°C. in a sealed tube acridine is hydrogenated in part to dihydroacridine (261).

Useful carboxyaldehyde and carboxylic acid derivatives of heterocyclic nitrogen compounds are obtained by reacting alkylated heterocyclic nitrogen compounds with selenium dioxide at moderate to high temperatures. Oxidations of this type are not much different from those shown by alkyl benzene derivatives, with the exception that the tertiary nitrogen appears to exert an activating

influence on an adjacent alkyl group. These oxidations are discussed from the viewpoint of the nitrogen system of compounds by Bergstrom (21a), who shows that the —N=CH— group in nitrogen ring compounds is comparable in many of its reactions to the aldehyde group in the oxygen system. The activating influence of this aldehydic nitrogen group is transmitted to some extent along the carbon chain. For example, Henze (95) was able to obtain small yields of the corresponding pyridinealdehydes and pyridinecarboxylic acids from the reaction of 2- and 3-methylpyridines with selenium dioxide. Kwartler and Lindwall (130) describe the preparation of quinoline-4-aldehyde derivatives in 50–60 per cent yield from 4-methylquinoline and 6-methoxylepidine, using selenium dioxide in xylene as solvent.

The alkyl group adjacent to the tertiary nitrogen apparently is considerably more active than an alkyl group in the β-position. According to a patent by Henze and Henze (96), it is possible to separate a mixture of α- and β-alkylated pyridines by means of selenium dioxide, since the α-derivative is attacked preferentially. In heterocyclic nitrogen compounds having several alkyl groups, the α-alkyl group also is attacked first. Burger and Modlin (31) oxidized 2,3,8-trimethylquinoline to 3,8-dimethylquinoline-2-aldehyde and 2,3,8-trimethyl-5-nitroquinoline to 3,8-dimethyl-5-nitroquinoline-2-aldehyde. Henze (95) reports that 2-ethyl-3-methylquinoline forms 3-methylquinoline-2-carboxylic acid, the ethyl group being destroyed.

In repeating some of the work on the preparation of quinolinealdehydes from the corresponding homologs by direct oxidation with selenium dioxide, Kaplan (125) found that the best yields are obtained when the selenium dioxide is prepared shortly before use. If the selenium is stored unsublimed for upward of several months, it converts quinaldine into a benzoin-type compound (quinaldoin) instead of the aldehyde, and lepidine into 1,2-di-4-quinolylethylene. This anomalous behavior does not appear to result because of the presence of selenates, nor is it a catalytic effect.

Other interesting types of nitrogen compounds reported to have been oxidized by selenium dioxide are listed in the following references: isoquinoline derivatives to isoquinaldehydes by Burrows and Lindwall (32); methylnaphthoxazole and methylbenzimidazole to naphthoxazole- and benzimidazole-2-carboxaldehydes in a patent to the I. G. Farbenindustrie A.-G. (110); and the oxidation of hydroquinine to hydroquininone by McKee and Henze (140).

While it has been known for some time that phenylhydrazine reduces selenium dioxide (101) and can be used for the analysis of selenite (90, 174), it is only recently that this reaction has been studied in detail to determine the products formed. Postowskii, Lugovkin, and Mandryk (188) have found that several types of compounds are obtained from arylhydrazines, depending on the reaction conditions. In acid solutions arylhydrazines react first to form a diazonium salt, and the course of the reaction can be followed by coupling the diazonium salt with β-naphthol to form the azo dye. (Using α-naphthylamine in place of β-naphthol, Feigl and Demant (70) have shown this reaction to be a sensitive spot test for determining arylhydrazines, hydrazones, and osazones.) On

continued refluxing with selenious dioxide in acid solution, phenylhydrazine produces some tetraphenyltetrazine and a blue dye. In like manner, *p*-nitrophenylhydrazine gives good yields of *p*-nitrophenyltriazine and the compound $p\text{-}O_2NC_6H_4N{=}NNHC_6H_4NO_2\text{-}p$. By the use of selenium dioxide in alcohol the reaction is modified still more, with diphenylamine being obtained in 94 per cent yield from phenylhydrazine.

5. Oxidation of sulfur compounds

Alkyl and aryl thiols (mercaptans), thiol acids, thioamides, dithiocarbamates, dithiophosphates, thiourea, and thiourea derivatives in which enolization to form the —SH group is possible, all undergo ready oxidation with selenium dioxide or selenite ion to form disulfides along with selenium compounds in some cases. This type of reaction finds use in the preparation of rubber accelerators and for the analysis of selenium. Organic sulfides are oxidized to sulfoxides and sulfones (152).

Painter (183) prepared an unstable compound of the type RSSeSR by reacting cysteine at low temperatures with selenium dioxide in a solvent. Similar compounds were made by Bersin (21b) from thioglycolic acid and glutathione. Painter believes that the reaction between a thiol and selenium dioxide is best interpreted as follows:

$$2RSH + SeO_2 \rightarrow RS{-}Se{-}SR + H_2O$$
$$\qquad\qquad\qquad\qquad\quad \downarrow$$
$$\qquad\qquad\qquad\qquad\quad O$$
$$4RSH + SeO_2 \rightarrow RSSeSR + RSSR + 2H_2O$$
$$\qquad\qquad\qquad\quad \downarrow$$
$$4RSH + SeO_2 \rightarrow 2RSSR + Se + 2H_2O$$

By reacting cysteine hydrochloride with sodium selenite Stekol (234) obtained selenium tetracysteine, $Se(SCH_2CHNH_2COOH)_4$. Tetravalent selenium compounds having useful vulcanization properties have been prepared by Russell (203) by treating secondary amines and carbon disulfide with selenium dioxide in an alcohol solvent. The dithiocarbamate formed from the secondary amine and carbon disulfide produces $(R_2NCS_2)_4Se$ in this reaction.

According to Werner (254) thiourea is oxidized to bis(aminoiminomethyl) disulfide by selenium dioxide, as shown by the following equation in which thiourea is written in the tautomeric form:

$$4NH_2{-}\overset{\overset{NH}{\|}}{C}{-}SH + H_2SeO_3 \rightarrow 2\left[NH_2\overset{\overset{NH}{\|}}{C}{-}S{-}\right]_2 + Se + 3H_2O$$

This reaction can be used for the quantitative analysis of selenious acid or thiourea or as a qualitative test for these substances, as shown by Falciola (66). Substituted thiourea derivatives, thioacetamide, and thiobenzamide appear to react in the same manner; consequently, Werner (255) proposed this as a qualitative test for the —SH group in organic compounds. Tetrasubstituted thiourea

compounds, as would be expected, do not react with selenium dioxide. A large number of substituted thiourea compounds were qualitatively examined for reaction with several metal ions and with selenite ion in an acid medium by Yoe and Overholser (260), who conclude that thiourea itself gives the most sensitive reaction.

Ivanov (114) first proposed the use of thiocyanate for the analysis of selenite and was able to isolate the unstable compound $(HSCN)_2 \cdot H_2SeO_3$ by adding selenious acid to an ammonium thiocyanate solution. This compound quickly changes over to free selenium. According to Ljung (136) and Hall (93) the reaction appears to be sensitive to one part of selenite in 20–38 million parts of solution if carried out in boiling hydrochloric acid solution. Ljung formulates the reaction as:

$$6H^+ + 2CNS^- + SeO_2 \rightarrow Se\ (s) + 2CN^- + 2S^- + H_2O$$

However, Hall believes that the principal products of the reaction are NH_4^+, CO_2, SO_4^{--}, and sulfur.

The use of a mixture of selenium dioxide and calcium chloride for differentiating various types of war gases has been suggested by Bradley (28). Liquid vesicants are brought in contact with the powder. In contact with droplets or a spray of Lewisite (β-chlorovinyldichloroarsine), the mixture becomes red instantly, owing to the reduction of selenium dioxide. Liquid "mustard gas" develops no red color until the powder is moistened with water, and in this case the maximum color intensity is not reached for about 5 min. Thiodiglycol reacts in the same manner.

6. Oxidation with selenium dioxide in concentrated sulfuric acid

The catalytic behavior of selenium and selenium dioxide in the medium of concentrated sulfuric acid has been discussed previously in the section of this paper relating to the mechanism of organic oxidations. It was also mentioned that practical use is being made of this property by employing selenium and selenium dioxide in sulfuric acid as catalysts for the rapid combustion of organic matter in the Kjeldahl method of analysis (29, 133, 165, 216). Another interesting application of this fact has been described recently by Woodward, Badgett, and Kaufman (259). These authors observe that selenium, selenium dioxide, and copper selenite function as effective catalysts in concentrated sulfuric acid for the liquid-phase oxidation of nicotine, β-picoline, and quinoline to nicotinic acid. At 250–330°C., and with a quantity of selenium catalyst equal to about 10 per cent by weight of the compound oxidized, the maximum yield of nicotinic acid obtained from either nicotine or quinoline is approximately 75 per cent of theoretical, and from β-picoline about 50 per cent of theoretical.

Long before the catalytic properties of selenium dioxide in sulfuric acid were recognized, a test was developed and widely used for the identification of alkaloids by their color reactions with this reagent. Studies of this reaction were made by Brandt (30), Dragendorff (57), Ferreira da Silva (73), Jouve (118), Lafon (131), Mecke (151), Orloff (181a), Schmidt (217), and Sergeeff (225a).

Conversely, spot tests were developed for the detection of selenite in sulfuric acid, using codeine phosphate (109, 192) and aspidospermine (184). Other compounds used for the same purpose were pyrrole (20, 213), diphenylamine (137), and acetylene (118).

More recent studies of Dewey and Gelman (55) dealing with the color reactions of nitrogen compounds have brought out the fact that color development with selenium dioxide in sulfuric acid is not a specific test for the alkaloids. This statement is supported by Levine (134), who similarly investigated the color reactions of phenols and phenolic ethers. Levine found that phenols brought in contact with concentrated sulfuric acid containing 0.5 per cent of selenium dioxide or 0.75 per cent of sodium selenite give rise to a color ranging from pale green to blue-green or purplish blue or the appearance of several colors simultaneously. On standing, or heating, or on the addition of water the characteristic color disappears and is replaced by a brown to brick-red color. The reaction appears to be very sensitive and widely applicable. The following types of phenols respond to the test: mono-, di-, and tri-phenols; phenolic ethers, aldehydes, alcohols, and acids; glycosides yielding phenols on hydrolysis; alkaloids having phenolic groups. Nitrated phenols give negative results. Levine explains the course of the reaction by saying that the phenolic body decomposes selenium dioxide to selenium and the latter dissolves in sulfuric acid with a green color owing to the formation of $SeSO_3$. This explanation probably is not tenable, since definite selenium compounds have been isolated (see table 1 of the following section) from reactions with selenium dioxide in sulfuric acid, as shown by Battegay and Hugel (15–17), Farbwerke vorm. M. L. G. B. (67, 68), and Zimmer & Cie (249). In any case, Levine concludes that color production appears to be a specific test for the phenolic hydroxyl group and that a positive reaction, therefore, cannot be accepted as indicative of the presence of the opium alkaloids unless other phenolic compounds are absent. This conclusion is modified further by Dewey and Gelman, who show that color production with the selenium dioxide reagent is not a specific reaction of phenolic compounds and that many nitrogenous compounds, especially those containing two or three aromatic nuclei, give intense color reactions with this reagent. The test provides a sensitive method for detecting and distinguishing between certain nitrogen compounds: for example, the colors produced by 1-naphthylamine, 2-naphthylamine, and di-2-naphthylamine can be readily distinguished; diphenylguanidine shows no color, but triphenylguanidine yields a pale blue changing to yellow. Dewey and Gelman declare that the test with selenium dioxide–sulfuric acid reagent for the presence of opium alkaloids cannot be considered conclusive unless interfering phenols and nitrogen compounds are known to be absent.

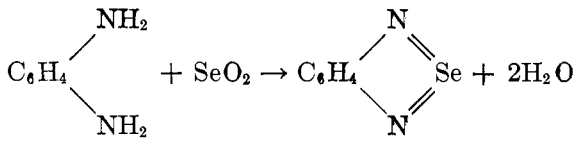
7. Reactions yielding organoselenium compounds

At several points in this discussion, attention has been directed to the fact that in many organic oxidations selenium dioxide appears to form addition compounds that decompose into oxidation products, complex organic selenium compounds, water, and selenium. Ordinarily only a small part of the selenium

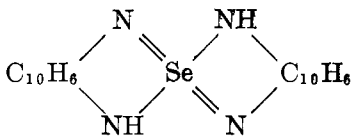
can be recovered in the organically bound form, but Zacharewicz (264) reports one case in which camphene selenide is the sole reaction product from camphene and selenium dioxide. The literature on selenium dioxide discloses other types of reactions that lead to the formation of organoselenium compounds. These are listed in table 1.

Organoselenium compounds have been prepared from selenium dioxide in the Grignard reaction (126), in the Friedel–Crafts synthesis (40, 51, 97, 139), and by the reaction of selenium dioxide with other organometallic compounds (155). Direct addition occurs with substituted butadiene hydrocarbons (9), certain quaternary ammonium compounds (38), oxalic acid (83), a benzidine–acetone mixture (72), alcohols (6, 52, 101, 190), aniline (6, 54), and piperidine (141, 142). The reactions of organic compounds with selenium dioxide in concentrated sulfuric acid to form selenopyronines (15–17), aromatic selenium compounds (67, 68), and alkaloid-selenium compounds (249) are interesting because of the light they throw on the mechanism of color reactions obtained with phenols, aromatic nitrogen compounds, and alkaloids in this reagent.

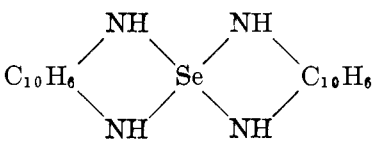
Aromatic *o*-diamines and related compounds react with selenious acid or selenium dioxide to form an interesting series of compounds known as the piaselenols (18, 75, 94, 99–101, 215). The reaction takes place in water or alcohol solution at ordinary temperatures with the formation of a stable five-membered heterocyclic ring as follows, according to Hinsberg (99):



Peri-naphthylenediamine reacts in a different manner to produce di-peri-naphthoselendiazole (102, 214)



and dihydrodi-peri-naphthoselendiazole (102):



The compound 1,3-dimethyl-2,6-dioxypiaselenolpurine

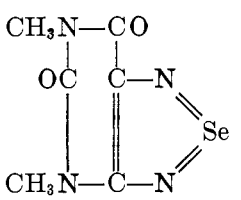


TABLE 1

Reactions with selenium dioxide yielding organic selenium compounds

NAME OF COMPOUND REACTED WITH SeO_2	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
Amylene		Addition compound	(154)
Butadiene	$CHCl_3$; low temperature	No reaction	(9)
Cyclohexene		Addition compound	(154)
2,3-Dimethylbutadiene	$CHCl_3$; low temperature	Cyclic selenone	(9)
3-Chloro-2-methylbutadiene	$CHCl_3$; low temperature	Cyclic selenone	(9)
2-*tert*-Butylbutadiene	$CHCl_3$; low temperature	Cyclic selenone	(9)
2,3-Di-*tert*-butylbutadiene	$CHCl_3$; low temperature	Cyclic selenone	(9)
2,3-Diphenylbutadiene	$CHCl_3$; low temperature	Cyclic selenone	(9)
1,2,3,4-Tetramethylbutadiene	$CHCl_3$; low temperature	Unstable product	(9)
2,3-Diethyl-1,4-dimethylbutadiene	$CHCl_3$; low temperature	Unstable product	(9)
Camphene	Reflux	Camphene selenide	(264)
Benzene	Friedel-Crafts synthesis	Diphenyl selenide, diphenyl diselenide, diphenylselenium dichloride, *p*-chlorophenyl selenide	(40, 139)
Toluene	Friedel-Crafts synthesis	Tritolylselenonium chloride	(51)
Anisole	Friedel-Crafts synthesis	Trianisylselenonium chloride	(97)
Phenetole	Friedel-Crafts synthesis	Triphenetylselenonium chloride	(97)
Resorcinol dimethyl ether	Friedel-Crafts synthesis	Mixture of products	(97)
Mercury dialkyls	50–60°C.	$(RHg)_2SeO_3$, R_2Se, R_2SeO	(155)
Triphenylphosphine	C_6H_6; room temperature	$(C_6H_5)_3PSe$ and $(C_6H_5)_3PO$	(155)
Triphenylarsine	C_6H_6; room temperature	$(C_6H_5)_3AsSe$ and $(C_6H_5)_3AsO$	(155)
Triphenylstibine	C_6H_6; room temperature	$(C_6H_5)_3SbSe$ and $(C_6H_5)_3SbO$	(155)
Ethyl bromide	Grignard synthesis	Ethyl acid selenite	(126)
Methanol	Low temperature	Methyl hydrogen selenite	(6)
Methanol	<200°C.	Dimethyl selenite	(153)
Ethanol	Low temperature	Ethyl hydrogen selenite	(101)

TABLE 1—*Continued*

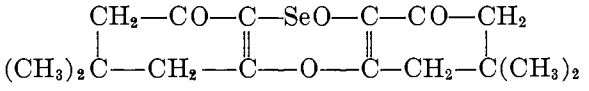
NAME OF COMPOUND REACTED WITH SeO_2	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
Ethanol	<200°C.	Diethyl selenite	(153)
1-Propanol	<200°C.	Di-*n*-propyl selenite	(153)
1-Butanol	<200°C.	Di-*n*-butyl selenite	(153)
Isobutyl alcohol	<200°C.	Diisobutyl selenite	(153)
Isoamyl alcohol	<200°C.	Diisoamyl selenite	(153)
Isoamyl alcohol and ammonia	Low temperature	Ammonium isoamyl selenite	(52)
Piperidine	Low temperature	Piperidine selenite	(141, 142)
Aniline	Low temperature	Unstable addition compound	(6, 54, 101)
Aniline sulfate	In H_2SO_4	Black crystals	(67)
Methylaniline	Low temperature	Unstable addition compound	(6)
p-Toluidine	Low temperature	Unstable addition compound	(6)
Benzidine and acetone	Low temperature	Ternary addition compound	(72)
Oxalic acid	Steam bath	$SeO_2 \cdot (COOH)_2$	(83)
Oxalic acid	See table 2		
$(CH_3)_4NCl$		$((CH_3)_4NCl)_2 \cdot SeO_2$	(38)
$(C_2H_5)_4NCl$		$((C_2H_5)_4NCl)_2 \cdot SeO_2$	(38)
Phenol	H_2SeO_3	$(HOC_6H_4)_2Se$	(240)
Phenol	In H_2SO_4	Colorless crystals	(67)
Phenoxyacetic acid	H_2SeO_3	$(C_6H_4OCH_2COOH)_2SeO$	(240)
Resorcinol	H_2SeO_3	Brown powder	(68)
Dimethyldihydroresorcinol	Methanol	Anhydromethon-selenium oxide	(26, 232)
Resorcinolarsonic acid	In H_2SO_4	Colorless product	(67)
β-Naphthol	Ethyl acetate	$(HOC_{10}H_6)_2Se$	(26)
Salicylic acid	In H_2SO_4	Colorless crystals	(67)
o-Nitrophenol	In H_2SO_4	Yellow product	(67)
p-Nitrophenol	In H_2SO_4	Yellow product	(67)
p-Acetaminophenetidine	In H_2SO_4	$(C_2H_5OC_6H_3NHCOCH_3)_3 \cdot SeSO_4 \cdot H_2O$	(67)
Antipyrine	In H_2SO_4	Diantipyryl selenide, $(C_{11}H_{11}ON_2)_2Se$	(67)
p-Nitroantipyrine	Formic acid	Di-*p*-nitroantipyryl selenide	(68)
p-Tolylantipyrine	Alcohol	Di-*p*-tolylantipyryl selenide	(68)
Ethylhydroquinine	In H_2SO_4	Selenoethylhydro-quinine	(249)
Ethylhydrocupreine	In H_2SO_4	Selenoethylhydro-cupreine	(249)
Hydrocupreine	In H_2SO_4	Selenohydrocupreine	(249)
Tetramethyldiamino-diphenylmethane	In H_2SO_4	Tetramethyl-2,6-di-aminoselenopyronine	(15, 16)

TABLE 1—*Continued*

NAME OF COMPOUND REACTED WITH SeO_2	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
Tetramethyldiaminodiphenylmethane derivatives	In H_2SO_4	Selenopyronines	(17)
o-Phenylenediamine	Water	Piaselenol	(99, 101)
Carboxy or sulfonic aromatic diamines	Water	Piaselenol derivatives	(94)
4-Methyl-1,2-phenylenediamine	Water	4-Methyl-1,2-piaselenol	(99)
4-Hydroxy-1,2-phenylenediamine	Water	4-Hydroxy-1,2-piaselenol	(75, 94)
1,2-Naphthylenediamine	Water and sodium acetate	Naphthylene-1,2-piaselenol	(99)
o-Tolylenediamine	In aqueous HCl	Methylchloropiaselenol	(100)
Peri-naphthylenediamine	In pyridine or methanol	Dihydrodi-peri-naphthoselendiazole	(102)
Peri-naphthylenediamine	In HCl–CH_3COOH solution	Di-peri-naphthoselendiazole	(102, 214)
o-$C_6H_5NHC_6H_4NH_2 \cdot HCl$	Water	Phenylpiaselenazonium chloride	(18)
1,3-Dimethyl-2,6-dioxy-4,5-diaminopyrimidine	Water	1,3-Dimethyl-2,6-dioxypiaselenolpurine	(215)
Thioglycolic acid	Selenite	$(HOOCCH_2S)_2Se$	(21b)
Cysteine		Cysteine–SeO_2 complex	(27, 183)
Cysteine hydrochloride	Na_2SeO_3	Selenium tetracysteine	(234)
Glutathione	Selenite	$(RS)_2Se$ compound	(21b)
Dithiocarbamates	Alcohol	Selenium dithiocarbamates	(203)
Mold growth	K_2SeO_3 and bread crumbs	Dimethyl selenide, $(CH_3)_2Se$	(23)
Mono- and di-butyldecalins.	$SeO_2 + Cl_2$ + ultraviolet light	Selenium-containing products(?)	(111)
Hydrogen cyanide	$(CH_3CO)_2O$; sealed tube	$Se(CN)_2$	(101)

has been prepared from 1,3-dimethyl-2,6-dioxy-4,5-diaminopyrimidine and selenious acid by Sachs and Meyerheim (215).

A reaction related to the formation of piaselenols is that reported by Stamm and Gossrau (232), in which dimethyldihydroresorcinol and selenium dioxide produce a compound having a stable six-membered ring, anhydromethonselenium oxide:



8. Physiological reactions of selenium dioxide

The toxicity of selenium compounds in general has been reviewed satisfactorily in a recent paper by Painter (183). From an industrial viewpoint this

subject has been discussed briefly in a review by one of the authors with Bearse and Shutt (252). For the purposes of this paper it is sufficient to add a few words regarding the toxicology of selenium dioxide.

Selenium dioxide appears to be somewhat more toxic than arsenic trioxide, and the symptoms observed upon ingestion are quite similar to those observed in arsenic poisoning. The animal body reduces selenium dioxide or selenite to harmless selenium, apparently either by the action of sulfur compounds of the tissue proteins or possibly by the glucose carried in the blood stream. The ingestion of selenites into the tissue of live rabbit ears and exposure of the injected region to ultraviolet irradiation causes the tissue to become discolored, owing to the deposition of red selenium. Urban (246) believes this discoloration to be caused largely by the reducing action of the —SH groups of the tissue proteins.

Selenious acid shows a definite corrosive action on the skin upon prolonged contact. Pringle (191) describes the cases of several workers exposed to selenium dioxide and selenious acid in industry who developed rashes or acutely painful paronychia but exhibited no alimentary or other systemic toxic symptoms. Such dermatoses were treated successfully in all but two of about twenty cases by removal of the patient from contact with the selenium compounds, by application of calamine lotion (*British Pharmacopeia*) several times a day, and by the use of ultraviolet irradiation. The wearing of rubber or cotton gloves and long-sleeved overalls is recommended as a protective measure. Any exposed parts should be washed frequently and thoroughly with soap and water. If this last injunction alone is obeyed, the ordinary laboratory worker handling selenium dioxide in small quantities probably never will develop a rash.

9. Analysis of selenium

Methods for the analysis of selenium in various types of compounds are treated adequately in the standard reference works. To complete this review of selenium dioxide reactions it is necessary only to list some of the more recent references pertaining to the analysis of selenium in organic compounds and in the form of selenites.

For the qualitative analysis of selenium in organic compounds Horn (109) suggests digesting 1 g. of the sample with 40 ml. of sulfuric acid and 0.2 g. of mercuric oxide until colorless, cooling, adding sulfuric acid, and testing 5 ml. of this solution with two drops of 3 per cent aqueous codeine sulfate. A green color changing to blue indicates selenium. The quantitative analysis of selenium in various types of organoselenium compounds has been discussed by Silverthorn (226) and by Painter (183).

Adams and Gilberton (1) describe a method for analyzing selenious acid and selenites by oxidizing them to selenate, using standard bromate solution, and determining the excess bromate by titration with standard arsenite solution. Selenium dioxide in air can be determined by the method of Chernyi (42), who suggests that air be passed through water to absorb the selenium dioxide, and the selenium estimated either colorimetrically by reduction with stannous

chloride solution or by the iodine–thiosulfate titration method. Heavy metals can be separated from selenite in alkaline solution by the use of alkaline hydroquinone and sodium sulfite, according to Geilmann and Wrigge (84). The

TABLE 2

Organic reagents used for the qualitative analysis of selenites

NAME OF COMPOUND USED	REACTION CONDITIONS	COLOR OBTAINED	REFERENCES
Pyrrole	H_3PO_4–$FeCl_3$	Blue	(20)
Pyrrole	Concentrated H_2SO_4	Blue	(213)
Codeine sulfate	Concentrated H_2SO_4	Green changing to blue	(109)
Codeine phosphate	Concentrated H_2SO_4	Green changing to blue	(192)
Aspidospermine	Concentrated H_2SO_4	Blue-green	(184)
Phenylhydrazine	Alcohol–water	Red selenium	(90, 174, 188)
as-Diphenylhydrazine	Glacial acetic acid	Red to violet	(71)
Phenyl semicarbazide	Alcohol–water	Red selenium	(174)
Polycyclic nitrogen compounds	Concentrated H_2SO_4	Various colors	(55)
Thiocyanates	HCl; hot solution	Red selenium	(93, 114, 136)
Thiourea	Acid solution	Red selenium	(66, 254)
Substituted thioureas	Acid solution	Red selenium	(255, 260)
Phenolic compounds	Concentrated H_2SO_4	Various colors	(55, 134)
Acetylene	Concentrated H_2SO_4	Red selenium	(118)
Glucose	Water	Red selenium	(236)
Rongalite			
Formaldehyde sulfoxylate	Acid medium	Red selenium	(244)
Formaldehyde sulfoxylate	Basic medium	Selenite reduced to colorless selenide	(244)
Oxalic acid	Sunlight, Fe(III)	$H_2SeO_3 + 2FeC_2O_4 + 2H_2C_2O_4 \rightarrow Fe_2(C_2O_4)_3 + 3H_2O + 2CO_2 + Se$	(69a)

conductometric analysis of selenite, using mercurous nitrate, has been studied by Kamecki (124). The equation for the reaction is as follows:

$$Na_2SeO_3 + Hg_2(NO_3)_2 \rightarrow Hg_2SeO_3 + 2NaNO_3$$

A list of organic reagents that have been suggested for use in spot tests and the qualitative analysis of selenites is given in table 2.

C. LIST OF ORGANIC COMPOUNDS OXIDIZED BY SELENIUM DIOXIDE (TABLE 3)

The compounds listed in table 3 are arranged according to the classification followed in the text of this article.

TABLE 3

List of organic compounds oxidized by selenium dioxide

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
1. Saturated compounds			
Ethane	350–400°C.	Glyoxal, acetic acid, and carbon dioxide	(198)
Alcohols	Low temperature	Alkyl acid selenites	(6, 101, 190, 251)
Alcohols	<200°C.	Dialkyl selenites	(7, 153)
Alcohols	300°C.	Corresponding aldehyde	(153)
Methanol	400°C.	Water and carbon dioxide	(64)
Ethanol	230°C.	Glyoxal; 5 per cent yield	(7)
Ethanol	400°C.	Water and carbon dioxide	(64)
1-Propanol	230°C.	Dialkyl selenite and complex products	(7)
1-Propanol	400°C.	Water and carbon dioxide	(64)
1-Butanol	230°C.	Dialkyl selenite and complex products	(7)
Tetrahydrofurfuryl alcohol	Reflux	No reaction	(182)
Menthol	Alcohol, reflux	Hydroxythymoquinone, thymol, and menthane	(106)
Borneol	Alcohol, reflux	Camphorquinone	(106)
Borneol	Reflux	Camphorquinone; 60 per cent yield	(3)
Isoborneol	Alcohol, reflux	Camphorquinone	(106)
Ethylene glycol	Reflux	No reaction	(54)
Glycerol	Reflux	No reaction	(54)
Ethyl ether	400°C.	Water and carbon dioxide	(64)
Ethyl iodide	K_2SeO_3	Ethanol	(163)
Formic acid	H_2SeO_4	Nothing isolated	(47)
Acetic anhydride	Reflux	Glyoxylic acid; 17 per cent yield	(101, 187)
Acetic anhydride	CH_3COOK at 60°C.	Dihydroxyacetic acid	(193)
Oxalic acid	H_2SeO_4	Nothing isolated	(47)
Propionic acid	Reflux	Pyruvic acid; 2 per cent yield	(54)
Malonic acid	H_2SeO_4	Nothing isolated	(47)
Gluconic acid	Reflux in water	No reaction	(54)
Lauric acid	Sealed tube; 300°C.	Undecene	(261)
Myristic acid	Sealed tube; 300°C.	Tridecylene	(261)
Palmitic acid	Sealed tube; 300°C.	Pentadecene	(261)
Stearic acid	Sealed tube; 300°C.	Heptadecene	(261)
Ethyl acetate	Reflux	Ethyl glyoxalate not obtained	(187)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
1. Saturated compounds—*Continued*			
Ethyl lactate	Reflux	Ethyl 2-keto-3-one-propionate	(8)
Diethyl malonate	Reflux	Ethyl mesoxalate	(7)
Diethyl malonate	Xylene; 130°C.	Diethyl dihydroxy-malonate and mono-ethyl dihydroxy-malonate	(177)
Diethyl succinate	170°C.	Ethyl hydrogen fumarate and fumaric acid	(7)
Diethyl malate	Excess ester	Ethyl diketosuccinate and ethyl fumarate	(6)
Diethyl malate	Excess SeO_2	Ethyl hydrogen mesoxalate and oxalic acid	(6)
Dimethyl tartrate	Reflux	Methyl fumarate	(8)
Diethyl tartrate	Reflux	Ethylketohydroxysuccinate	(8)
Dibutyl tartrate	Reflux	Nothing isolated	(8)
Diamyl tartrate	Reflux	Nothing isolated	(8)
2(a) Unsaturated aliphatic compounds			
Acetylene	220–240°C.	Carbon dioxide and 6 per cent glyoxal	(198)
Acetylene	400°C.	Water and carbon dioxide	(64)
Acetylene	Concentrated H_2SO_4	Nothing isolated	(118)
1-Heptyne		3-Hydroxy-1-heptyne; 27 per cent yield	(242)
1-Heptyne	Excess SeO_2	Some $C_4H_9COC{\equiv}CH$	(242)
1-Octyne		3-Hydroxy-1-octyne	(242)
Olefins	Selenite catalysts	Glycols and oxides	(68)
Ethylene	220–240°C.	Glyoxal; 80 per cent yield	(24, 195, 197, 198)
Ethylene	400°C.	Water and carbon dioxide	(64)
Propylene	220–240°C.	Methylglyoxal; 19 per cent yield	(198)
Butadiene derivatives	Low temperature	Cyclic selenones (see table 1)	(9)
1,3-Pentadiene	H_2O_2 + SeO_2	Yields 1,2-diols	(225)
2-Pentene	Sealed tube	Complex products	(198)
2-Pentene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	2-Penten-4-ol	(89)
2-Methyl-2-butene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	2-Methyl-2-buten-1-ol	(88, 89)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
2(a) Unsaturated aliphatic compounds			
Trimethylethylene	Benzene	Mechanism of oxidation	(89)
1-Hexene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	2-Hexen-1-ol and 1-hexen-3(?)-ol	(89)
2-Methyl-2-pentene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	2-Methyl-2-penten-1-ol	(87, 89)
3-Methyl-2-pentene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	3-Methyl-3-penten-2-ol	(89)
3-Methyl-2-pentene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	3-Methyl-3-penten-2-ol	(87, 89)
2,3-Dimethyl-3-pentene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	2-Isopropyl-2-buten-1-ol	(89)
2,2,3-Trimethyl-3-pentene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	2-tert-Butyl-2-buten-1-ol	(89)
3-Nonene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	Mixture of nonenols	(89)
4-Nonene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	Mixture of nonenols	(89)
β-Methylallyl alcohol	Hexyl alcohol or dioxane	β-Methylacrolein; 50–60 per cent yield	(127)
Unsaturated fatty acids	H_2SeO_3; 100°C.	Double bond preserved	(78)
Oleic acid	Benzene under pressure	Double bond preserved	(223)
Castor oil	H_2SeO_3; 100°C.	White powder	(78)
Linseed oil	Ethanol reflux	Double bonds preserved	(245)
Cottonseed oil	Ethanol reflux	Double bonds preserved	(245)
Olive oil	Ethanol reflux	Double bonds preserved	(245)
Unsaturated aliphatic–aromatic combinations (see section 2(d))			
2(b) Unsaturated alicyclic compounds			
Cyclopentene	$(CH_3CO)_2O$ reflux	Cyclopentenol and diol	(53)
Methylcyclopentene	$(CH_3CO)_2O$; 100°C.	Methylcyclopentenol and methylcyclopentenyl methylcyclopentenone	(53)
Methylcyclopentene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	1-Ethylcyclopenten-5-ol	(89)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
2(b) Unsaturated alicyclic compounds—*Continued*			
Cyclopentadiene	H_2O_2 + SeO_2	Yields 1,2-diol	(225)
Cyclohexene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	1-Cyclohexen-3-ol	(89)
Cyclohexene	Alcohol reflux	Cycloölefin ketone	(221–224)
Cyclohexene	H_2O_2 + SeO_2	*trans*-Cyclohexanediol; 45 per cent yield	(225)
1-Methylcyclohexene	Alcohol reflux or H_2SeO_3 autoclave	Cycloölefin ketone	(221–224)
1-Methylcyclohexane	Alcohol reflux	1-Methylcyclopenten-6-ol (30–40 per cent yield) and some 1-methylcyclopenten-6-one	(247)
1-Methylcyclohexene	Water reflux	Mostly 1-methylcyclopenten-6-one	(247)
1-Methylcyclohexene	CH_3COOH reflux	1-Methylcyclopenten-6-ol acetate; 40 per cent yield	(247)
3-Methylcyclohexene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	6-Methylcyclohexanol, 4-methylcyclohexene, 4-methylcyclohexen-3-ol, toluene	(89)
4-Methylcyclohexene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	4-,5-, and 6-Methylcyclohexen-3-ol, 4-isomer predominating	(89)
1-Ethylcyclohexene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	1-Ethylcyclohexen-6-ol; 30–40 per cent yield	(88, 89)
1,2-Dimethylcyclohexene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	First fraction: *o*-xylene and 2,3-dimethyl-1,3-cyclohexadiene Second fraction: one ethylenic and one dienic alcohol	(89)
1,6-Dimethylcyclohexene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	Five fractions: each containing *o*-xylene and 2,3-dimethyl-1,3-cyclohexadiene	(89)
1,1,4-Trimethylcyclohexene		Trimethylcyclohexen-5-one	(12)
Δ^1-Menthene		Carvotanacetone	(25, 221–224)
Δ^3-Menthene		Δ^3-Menthen-5-one	(25, 221–224)
Carvomenthene		Carvotanacetone	(239)
α-Phellandrene		Cuminaldehyde and *p*-cymene	(25, 104)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
2(b) Unsaturated alicyclic compounds—*Continued*			
Dipentene		Carvone, *p*-cymene, and *p*-tolyl methyl ketone	(105)
Dipentene		Carvone	(221–224)
2(c) Unsaturated polycarbocyclic compounds			
Indene	Sealed tube; 300°C.	Hydrindene	(261)
Tetralin	Reflux or solvents	Bright red *o*(?)-diquinone	(251)
$\Delta^{9,10}$-Octalin	$(CH_3CO)_2O$; 5°C.	$\Delta^{9,10}$-Octalol-1 acetate	(37)
$\Delta^{9,10}$-Octalin	$(CH_3CO)_2O$; 30°C.	$\Delta^{9,10}$-Octalindiol-1,5 diacetate	(37)
$\Delta^{9,10}$-Octalin	$(CH_3CO)_2O$; 120°C.	1,2,3,6,7-Hexahydronaphthalenediol-1,5 diacetate	(37)
Pinene	Reflux	Myrtenol, myrtanol, β-pinene, and 1,5-pinadiene	(60)
Pinene	Alcohol reflux	Myrtenol, myrtanol	(61)
Pinene		Methyl group in pinene oxidized; some myrtenyl selenide	(264)
α-Pinene	Alcohol reflux	Verbenone; 35 per cent yield	(59, 220, 222–224)
β-Pinene	Alcohol reflux	Pinocarvone; 35 per cent yield	(59, 222–224)
β-Pinene		Pinocarveol and pinocarvone	(265)
β-Pinene	Various solvents; SeO_2 in molar ratio	Carvopinone with some pinocarvone	(230)
β-Pinene	Alcohol; 0.5 mole SeO_2	Pinocarveol (30 per cent yield); some carvopinone	(117, 231)
β-Pinene	CH_3COOH reflux	Pinocarveol; pinocarvyl acetate, carvopinone, and pinocarvone	(231)
Camphene	Reflux	Camphene selenide	(264)
Dihydro-α-dicyclopentadiene	CH_3OH; H_2SeO_3	Methyl ether of dihydro-α-dicyclopentadienol	(2)
Dihydro-α-dicyclopentadiene	C_2H_5OH; H_2SeO_3	Ethyl ether of dihydro-α-dicyclopentadienol	(2)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
2(c) Unsaturated polycarbocyclic compounds—*Continued*			
Dihydro-α-dicyclopentadiene	$C_5H_{11}OH$; H_2SeO_3	Amyl ether of dihydro-α-dicyclopentadienol	(2)
Dihydro-α-tricyclopentadiene	$(CH_3CO)_2O$; H_2SeO_3	Acetate of dihydro-α-tricyclopentadien-3-ol	(2)
Dihydro-β-tricyclopentadiene	$(CH_3CO)_2O$; H_2SeO_3	Acetate of dihydro-β-tricyclopentadien-3-ol	(2)
2(d) Aromatic compounds			
Phenol	Low temperature	Tarry resin (however, see table 1)	(54)
o-Cresol	Low temperature	Tarry resin	(54)
p-Cresol	Low temperature	Tarry resin	(54)
Toluene	Sealed tube; 300°C.	Benzoic acid; 27.4 per cent yield	(54)
Benzyl alcohol	Reflux	Benzaldehyde; approximately 100 per cent yield	(7)
Benzyl chloride	Reflux	Benzaldehyde; 49 per cent yield	(76)
Benzyl chloride	Reflux	Benzaldehyde and benzoic acid	(163)
p-Nitrobenzyl bromide	140–150°C.	*p*-Nitrobenzaldehyde and benzaldehyde	(76)
p-Nitrobenzyl chloride	Alcohol; 140–150°C.	2-Nitrobenzaldehyde; 56 per cent yield	(76)
p-Nitrobenzal bromide		*p*-Nitrobenzoic acid	(76)
2,4-Dinitrotoluene	Alcohol reflux	No reaction	(76)
2,4,6-Trinitrotoluene	Alcohol reflux	No reaction	(76)
Styrene	Sealed tube	Nothing isolated	(198)
Styrene	180–250°C.	Phenylglyoxal	(251)
Methylphenylacetylene	Reflux	Product hydrated in alkaline solution to $C_2H_5COC_6H_5$	(243)
Ethylphenylacetylene	Reflux	$CH_3CHOHC{\equiv}CC_6H_5$	(243)
3-Phenyl-2-pentene	CH_3COOH + $(CH_3CO)_2O$; 120–140°C.	3-Phenyl-3-penten-2-ol	(89)
Eugenol	Benzene; pressure	Double bond in side chain preserved	(223)
Acetisoeugenol	Alcohol; 50°C.	Trace of vanillin	(54)
Safrole		α-Ketodihydrosafrole; ethoxysafrole	(257)
		β-Ketodihydrosafrole; piperonylacrolein	

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
2(d) Aromatic compounds—*Continued*			
Isosafrole		Dihydrosafrole, ethoxysafrole; piperonylacrolein A new oxide and a new selenide	(257)
Ethyl phenylacetate	Reflux	Ethyl benzoylformate; 34 per cent yield	(6)
Ethyl mandelate	Reflux	Ethyl benzoylformate; 60 per cent yield	(6)
Ethyl β-phenylpropionate	Reflux	β-Phenylpropionic and cinnamic acids	(6)
5,6-Dimethoxyhomophthalic acid	Xylene	5,6-Dimethoxyphthalonic acid	(41)
Diphenylmethane	Reflux	Benzophenone; 87 per cent yield	(187)
Diphenylmethane	Reflux	Benzophenone; 47 per cent yield	(76)
4,4′-Dinitrodiphenylmethane	Dioxane	No reaction	(76)
Tolane	280°C.	Benzil; 35 per cent yield	(187)
Stilbene		Benzil; 86.6 per cent yield	(6)
Stilbene	235°C.	Benzil; 17 per cent yield	(187)
Dibenzyl	Sealed tube; 300°C.	Benzil and stilbene	(54)
Dibenzyl		Benzil; 33 and 17.5 per cent yields	(6)
Benzyl *p*-tolyl sulfone		No reaction	(48)
2,2-Dimesitylvinyl alcohol		Mesitil	(82)
Anthracene	Melt	Anthraquinone; 76 per cent yield	(187)
Anthracene	$C_6H_5NO_2$	Anthraquinone; 73 per cent yield	(6)
Phenanthrene	280°C.	Phenanthraquinone; 3 per cent yield	(187)
Phenanthrene		Phenanthraquinone; very little	(6)
Fluorene		Fluorenone; 5 per cent yield	(187)
Acenaphthene	CH_3COOH; 150–200°C.	Acenaphthylene glycol, acenaphthylene, dinaphthylenecyclobutane, polyacenaphthylene	(173)
Triphenylmethane	Reflux	Triphenylcarbinol; 15 per cent yield	(76)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
2(d) Aromatic compounds—*Continued*			
Tetraphenylethylene	220–230°C.	Nothing isolated	(187)
1,1,6,6-Tetraphenyl-1,5-hexadiene	CH_3COOH and H_2SeO_3	Tetraphenylhexatriene	(218)
1,6-Dibiphenylene-1,5-hexadiene	CH_3COOH and $C_6H_5OCH_3$	1,6-Dibiphenylene-hexatriene	(218)
Hexaphenylbutyne		Nothing isolated	(187)
2-Methyl-1,1′-dinaphthyl ketone	$C_6H_5NO_2$ at 230°C.	2-Carboxy-1,1′dinaphthyl ketone	(49)
1,2,5,6-Dibenzfluorene		1,2,5,6-Dibenzfluorenone	(10)
2-Methylbenzanthrone	H_2SeO_3; 230–240°C.	Benzanthrone-2-aldehyde	(121–123)
6-Methylbenzanthrone	H_2SeO_3; 230–240°C.	Benzanthrone-6-aldehyde	(121–123)
9-Methylmesobenzanthrone	H_2SeO_3; 230–240°C.	Mesobenzanthrone-9-aldehyde; 20 per cent yield	(50)
10-Methylmesobenzanthrone	$C_6H_5NO_2$; 230–240°C.	Mesobenzanthrone-10-aldehyde; 25 per cent yield	(50)
2-Benzylbenzanthrone	H_2SeO_3; 230–240°C.	2-Benzoylbenzanthrone	(121–123)
Indeno-2,3,2,1-benzanthrone	H_2SeO_3; 230–240°C.	1″-Ketoindeno-2″,3″, 2′,1′-benzanthrone; 100 per cent	(237)
Dihydro-2,3,2,1-benzanthrone	H_2SeO_3; 230–240°C.	1″-Ketoindeno-2″,3″, 2′,1′-benzanthrone	(237)
5-Methylnaphthanthraquinone	H_2SeO_3; 230–240°C.	Naphthoanthraquinone-5-carboxaldehyde, naphthoanthraquinone-5-carboxylic acid	(121–123)
1,5-Dibenzoyl-2,6-dimethylnaphthalene	$C_6H_5NO_2$; 230–240°C.	1,5-Dibenzoylnaphthalene-2,6-dicarboxylic acid	(121–123)
2(e) Complex unsaturated compounds			
Sterols and bile acids:			
Bile acids		Qualitative test	(35)
Apocholic acid		β-Dihydroxycholadienic acid	(34)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
2(e) Complex unsaturated compounds—*Continued*			
Sterols and bile acids—Cont.:			
Methylapocholate		β-Dihydroxycholadienic acid	(34)
Methyl-3(β)-acetoxy-$\Delta^{20,22}$-norallocholenate	$(CH_3CO)_2O$	3(β)-Acetoxy-21-hydroxy-$\Delta^{20,22}$-norallocholenic acid lactone	(210)
3,12-Diketocholanic acid	CH_3COOH; 100°C.	Qualitative test	(235)
Clionastrol		4,5-Cliostene-3,6-diol, $C_{29}H_{50}O_2$	(21)
Cholesterol	Se at 230°C.	Cholestanone; 30–40 per cent yield	(56)
Cholesterol		Two isomeric cholestenediols	(33)
Cholesterol		Metacholesterol	(175)
Cholesterol	CH_3COOH or $C_6H_5NO_2$	*cis*-$\Delta^{5,6}$-Cholestene-3,4-diol	(202)
Cholesteryl acetate	CH_3COOH	*cis*-$\Delta^{5,6}$-Cholestene-3,4-diol diacetate but mostly *trans*-cholestene-3,4-diol diacetate	(202)
Cholesteryl benzoate	CH_3COOH	*cis*-$\Delta^{5,6}$-Cholestene-3,4-diol (3-benzoate)	(202)
$\Delta^{3,14}$-Cholestene	Alcohol reflux	$\Delta^{3,14}$-Cholestadiene	(63)
4-Cholesten-3-one	CH_3COOH; 100°C.	Qualitative test	(235)
4-Cholestene-3,6-dione	CH_3COOH; 100°C.	Qualitative test	(235)
Cholestanone	C_2H_5OH	Cholestan-2,3-dione	(235)
Cholestan-6-one	CH_3COOH; 100°C.	Qualitative test	(235)
Cholestan-3-ol-6-one	CH_3COOH; 100°C.	Qualitative test	(235)
Cholestane-3,6-dione	CH_3COOH; 100°C.	Qualitative test	(235)
Coprostanone	C_2H_5OH	Slight reaction	(235)
Ergosterol		Dehydroergosterol	(35)
Dihydroergosterol		Dihydroergosterol oxide	(35)
Sitosteryl acetate	Benzene	4- and 6-hydroxysitosteryl acetates	(145)
Stigmasteryl acetate	$(CH_3CO)_2O$	4-Hydroxystigmasterol diacetate	(146)
Lanosteryl acetate	Alcohol	Isomeric diols	(19)
Dihydrolanosteryl acetate	CH_3COOH reflux	Lanosterol acetate	(19)
3′-Keto-4,6-dimethoxy-1,2-cyclopentenonaphthalene	CH_3COOH reflux	2′,3′-Diketo-4,6-dimethoxy-1,2-cyclopentenonaphthalene	(148)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
2(e) Complex unsaturated compounds—*Continued*			
Hormones:			
Δ^4-Androsten-17-ol.....		Δ^5-Androsten-3-one-17-ol	(228)
Δ^5-Androstene-3,17-diol diacetate.....	H_2SeO_3	Δ^5-Androstene-3,4,17-triol	(144)
Δ^5-Androstene-3,17-diol....	CH_3COOH	Δ^5-Androstene-3,4,17-triol	(144)
trans-Dehydroandrosterone.....		3,4-Dihydroxy-$\Delta^{5,6}$-androsten-17-one and 3,6-dihydroxy-$\Delta^{5,6}$-androsten-17-one	(227)
Δ^5-Pregnene-3,20-diol diacetate.....	CH_3COOH and benzene	Δ^5-Pregnene-3,4,20-triol	(144)
3,17-Dihydroxy-21-oxo-$\Delta^{5,6}$-pregnene.....		$\Delta^{5,6}$-3,4,17,20,21-Pregnenepentol Δ^4-3,6,17,20,21-Pregnenepentol	(227)
Pregnane carbonyl compounds.....		Pregnane polycarbonyl compounds	(164)
Estradiol.....		Cyclopentane ring of estradiol is broken	(108)
Polyterpenes:			
Lupeol.....	Benzene	Lupenol	(116)
Lupeol.....		Lupenalol	(211)
Betulin diacetate.....	CH_3COOH	Diacetoxylupenal	(205)
β-Amyrin acetate.....	CH_3COOH	β-Amyradinenol acetate and β-amyradienedionol acetate	(208)
β-Amyrin acetate.....	Dioxane	β-Amyradinenol acetate and β-amyradienedionol acetate	(208)
β-Amyranonal acetate.....		enol-β-Amyranedionol acetate	(206)
β-Amyradienyl-1-acetate...		β-Amyrenonyl acetate and $C_{32}H_{48}O_4$ or $C_{32}H_{46}O_4$	(185)
β-Amyrenonyl acetate.....	CH_3COOH	O_5 acetate	(176)
β-Amyradienonyl acetate..	CH_3COOH	O_5 acetate	(176)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
2(e) Complex unsaturated compounds—*Continued*			
Polyterpenes—Cont.:			
β-Amyradienonyl benzoate	CH_3COOH	$C_{37}H_{38}O_5$ (O_5 benzoate)	(176)
β-Amyrenonyl benzoate	CH_3COOH	$C_{37}H_{38}O_5$ (O_5 benzoate)	(176)
Isonoragathenol acetate		Product dehydrogenates to α,β-unsaturated ketone	(204)
Methyl ketoacetylolean olate		$C_{33}H_{46}O_7$	(176)
Methyl acetyldeoxyglycyrrhetate	CH_3COOH	Methyl acetyldehydrodioxyglycyrrhetate	(22)
Methyl acetyldesoxoglycyrrhetinate	CH_3COOH	Methyl acetyldihydrodesoxoglycyrrhetinate	(207)
Methyl acetyldesoxoglycyrrhetinate	Dioxane	Methyl acetyl-β-amyradienedionolate	(207)
Miscellaneous:			
Sarsapogenin esters	CH_3COOH	Halogenated side chain unaffected by SeO_2	(143)
Tetrahydrodiosgenin triacetate	CH_3COOH; benzene	Product similar to Δ^5-3,4-dihydroxycholestene	(147)
Tetrahydroösajetin trimethyl ether	CH_3COOH	Tetrahydroösajetinone trimethyl ether	(258)
Tetrahydropomiferitin tetramethyl ether		Tetrahydropomiferitone tetramethyl ether	(258)
Abietic acid		Dehydroabietic acid	(136a)
3. Aldehydes and ketones			
Aldehydes	Kinetics and mechanism of oxidation		(154, 157)
Acetaldehyde		Glyoxal; almost 100 per cent yield	(200)
Acetaldehyde	CH_3COOH–dioxane	Glyoxal; 72–74 per cent as bisulfite	(201)
Acetaldehyde	95 per cent CH_3COOH	Kinetics of oxidation	(157)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
	3. Aldehydes and ketones—*Continued*		
Propionaldehyde	95 per cent CH_3COOH	Kinetics of oxidation	(157)
Propionaldehyde		Methylglyoxal; 30 per cent yield	(200)
Butyraldehyde		Ethylglyoxal: 45 per cent yield	(200)
Butyraldehyde	95 per cent CH_3COOH	Kinetics of oxidation	(157)
Butyraldehyde acetal	95 per cent CH_3COOH	Mechanism of oxidation	(154)
Isobutyraldehyde	95 per cent CH_3COOH	Mechanism of oxidation	(157)
Heptaldehyde	95 per cent CH_3COOH	Mechanism of oxidation	(157)
Crotonaldehyde	Sealed tube	Nothing isolated	(198)
Crotonaldehyde	Methanol	β-Methoxy-α-ketobutyraldehyde	(193)
Crotonaldehyde dimethyl acetal	Methanol	β-Methoxy-α-ketobutyraldehyde	(193)
Crotonaldehyde	Ethanol	β-Ethoxy-α-ketobutyraldehyde	(193)
Crotonaldehyde	$(CH_3CO)_2O$ and H_2SeO_3	β-Acetoxy-α-ketobutyraldehyde	(193)
Crotonaldehyde	CH_3COOH and H_2SeO_3	Polymeric β-hydroxy-α-ketobutyraldehyde	(193)
Crotonaldehyde	CH_3COOH (35); $(CH_3CO)_2O$ (65)	Diacetate	(193)
Crotonaldehyde	CH_3COOH (80); $(CH_3CO)_2O$ (20)	Diacetate and β-acetoxy-α-ketobutyraldehyde	(193)
Crotonaldehyde	CH_3COOH (95); $(CH_3CO)_2O$ (5)	Diacetate and β-acetoxy-α-ketobutyraldehyde	(193)
Benzaldehyde	H_2SeO_4; alcohol	Selenic acid is reduced	(47)
Phenylacetaldehyde		Phenylglyoxal; 35 per cent yield	(200)
Cinnamaldehyde	Sealed tube	Nothing isolated	(198)
Cinnamaldehyde	Sealed tube	Hydrocinnamic acid	(261)
Levulose	Acid solution	H_2SeO_3 is reduced easily; glucose, maltose, and lactose show no reaction	(200)
Sucrose	Acid solution	Reduces H_2SeO_3 on prolonged boiling	(200)
Sucrose	H_2SeO_3	Velocity of inversion by H_2SeO_3 studied	(126)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
3. Aldehydes and ketones—*Continued*			
Ketones	.75 per cent CH_3COOH	Kinetics and mechanism of oxidation of the following ketones were studied: acetone; ethyl methyl, methyl propyl, isopropyl methyl, hexyl methyl, diethyl, dipropyl, diisopropyl, dibutyl, methyl phenyl, ethyl phenyl, and propyl phenyl ketones; pinacolone; cyclohexanone; 1,2- 1,3-, and 1,4-methylcyclohexanones	(154, 156)
Ketones	Alcohol solvents	Rates of oxidation of acetone, ethyl methyl ketone, and methyl propyl ketone in absolute and aqueous methanol, ethanol, 1-butanol, isobutyl alcohol, and isoamyl alcohol	(158)
Isomeric amyl methyl ketones	75 per cent CH_3COOH	Kinetics of oxidation	(160)
Isomeric methyl hexyl ketones	75 per cent CH_3COOH	Kinetics of oxidation	(160)
Substituted acetophenones	75 per cent CH_3COOH	Kinetics of oxidation of *m*-$NO_2C_6H_4COCH_3$, *p*-$BrC_6H_4COCH_3$, *p*-$ClC_6H_4COCH_3$, *p*-$CH_3OC_6H_4COCH_3$, *p*-$CH_3C_6H_4COCH_3$, *p*-$IC_6H_4COCH_3$, and $C_6H_5CH_2COCH_3$	(158)
Acetone	Reflux	Methylglyoxal	(92, 194, 196, 200)
Ethyl methyl ketone	Reflux	Ethylglyoxal and small amount of diacetyl	(200)
Diethyl ketone	Reflux	Ethylmethylglyoxal	(200)
Acetylacetone	C_2H_5OH	Triketopentane; 12 per cent yield	(36, 200)
Acetylacetone	C_2H_5OH	Triketopentane; 30 per cent yield	(186)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
3. Aldehydes and ketones—*Continued*			
Acetonylacetone		Diacetylethylene; 15 per cent yield	(4)
Ethyl acetonedicarboxylate		Ethyl α,β-diketobutyrate	(6)
Ethyl acetoacetate	Xylene	Ethyl α,β-diketobutyrate	(177)
Triacetone mannitol		Mechanism of oxidation	(156)
Pinacolone		*tert*-Butylglyoxal; 48 per cent yield	(80)
Cyclopentanone	Reflux	Cyclopentane-1,2-dione	(200)
Methylcyclopentanone	CH_3COOH	Methylcyclopentanedione	(53)
Cyclohexanone	Reflux	Cyclohexane-1,2-dione and some adipic acid	(200)
1-Methyl-4-cyclohexanone	C_2H_5OH	1-Methyl-3,4-cyclohexanedione and 3-ethoxy-Δ^5-cyclohexen-4-one	(85)
1-Methyl-3-cyclohexanone	C_2H_5OH	Similar results	(85)
1-Methyl-2-cyclohexanone	C_2H_5OH	1-Methyl-Δ^6-cyclohexene-2,3-dione	(85)
Cycloheptanone	C_2H_5OH	1,2-Cycloheptanedione	(85)
Cycloöctanone	C_2H_5OH	8-Ethoxy-1,2-cycloöctanedione	(85)
Acetophenone		Phenylglyoxal	(196, 199, 200)
Propiophenone		Phenylmethylglyoxal	(200)
Benzyl methyl ketone	C_2H_5OH	Unidentified compound; no $CH_3COCOC_6H_5$	(186)
Acetomesitylene	Dioxane	Mesitylglyoxal; 82.5 per cent yield	(86)
Benzyl isoduryl ketone	Dioxane	Isoduryl phenyl diketone; 81 per cent yield	(79)
Di(β-isoduryloyl)methane	Dioxane	Dimesityl triketone	(81)
1,3-Diketohydrindene	Dioxane	Ninhydrin; 35 per cent yield	(240a)
Isoketopinic acid	CH_3COOH	*o*-Oxoisoketopinic acid	(113)
Benzyl phenyl ketone	$(CH_3CO)_2O$ reflux	Benzil; 86 per cent yield	(93a)
Benzyl 4-chlorophenyl ketone	$(CH_3CO)_2O$ reflux	4-Chlorobenzil; 94 per cent yield	(93a)
Benzyl 4-bromophenyl ketone	$(CH_3CO)_2O$ reflux	4-Bromobenzil; 95 per cent yield	(93a)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
3. Aldehydes and ketones—*Continued*			
Benzyl *p*-tolyl ketone	$(CH_3CO)_2O$ reflux	4-Methylbenzil; 75 per cent yield	(93a)
Benzyl o-4-xylyl ketone	$(CH_3CO)_2O$ reflux	3,4-Dimethylbenzil; 95 per cent yield	(93a)
Benzyl *m*-4-xylyl ketone	$(CH_3CO)_2O$ reflux	2,4-Dimethylbenzil	(93a)
Benzyl *p*-xylyl ketone	$(CH_3CO)_2O$ reflux	2,5-Dimethylbenzil; 90 per cent yield	(93a)
Benzyl mesityl ketone	$(CH_3CO)_2O$ reflux	2,4,6-Trimethylbenzil; 92 per cent yield	(93a)
Benzyl 4-diphenylyl ketone	$(CH_3CO)_2O$ reflux	4-Phenylbenzil; 95 per cent yield	(93a)
2,4,6-Triisopropylacetophenone	Wet dioxane	2,4,6-Triisopropylphenylglyoxal; 82 per cent yield	(81a)
Propiomesitylene	Wet dioxane	Mesityl methyl diketone; 42 per cent yield	(81a)
3-Nitroacetomesitylene	Wet dioxane	3-Nitromesitylglyoxal; 72 per cent yield	(81a)
3-Bromoacetomesitylene	Wet dioxane	3-Bromomesitylglyoxal; 65 per cent yield	(81a)
3-Bromo-5-nitroacetomesitylene	Wet dioxane	3-Bromo-5-nitromesitylglyoxal; 90 per cent yield	(81a)
Mesityl *p*-nitrobenzyl ketone	Wet dioxane	Mesityl *p*-nitrophenyl diketone; 72 per cent yield	(81a)
Mesityl *m*-nitrobenzyl ketone	Wet dioxane	Mesityl *m*-nitrophenyl diketone; 81 per cent yield	(81a)
p-Bromobenzyl mesityl ketone	Wet dioxane	Mesityl *p*-bromophenyl diketone; 72 per cent yield	(81a)
Menthone	C_2H_5OH	Hydroxythymoquinone	(103)
Piperitone		Thymol and oxythymoquinone	(104)
Camphor	$(CH_3CO)_2O$, dioxane	Camphorquinone; 65 per cent yield	(3)
Camphor	$(CH_3CO)_2O$; 140–150°C.	Camphorquinone; good yield	(65)
Camphor	C_2H_5OH	Camphorquinone; 27 per cent yield	(248)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
3. Aldehydes and ketones—*Continued*			
Camphor	Toluene or xylene	Camphorquinone; 88–90 per cent yield	(248)
Camphor	$(CH_3CO)_2O$	Camphorquinone; 95 per cent yield	(248)
l-Epicamphor	$(CH_3CO)_2O$	Camphorquinone	(5)
d-Epicamphor	$(CH_3CO)_2O$	Camphorquinone	(5)
α-Hydroxycamphor	C_2H_5OH	Camphorquinone; 40 per cent yield	(248)
α-Hydroxycamphor	No solvent	Camphorquinone; 85 per cent yield	(248)
α-Chlorocamphor	No solvent	Camphorquinone; 30 per cent yield	(248)
α-Bromocamphor	No solvent	Camphorquinone; 55 per cent yield	(248)
Ethylcamphor	No solvent	Camphorquinone; 12 per cent yield and some ethylene-camphor	(248)
Benzylcamphor	No solvent	Benzylidenecamphor; 95 per cent yield	(248)
Isonitrosocamphor	85°C.	Camphornitrile (23 per cent) and camphoric anhydride (27 per cent)	(248)
Isonitrosocamphor	Alcohol	Camphornitrile (20 per cent) and camphoric anhydride (12 per cent)	(248)
Isonitrosocamphor	Toluene	Camphornitrile (36 per cent) and camphoric anhydride (36 per cent)	(248)
4-*p*-Nitrophenylcamphor	$(CH_3CO)_2O$	4-*p*-Nitrophenyl-camphorquinone	(179)
2-Methyl-1,4-naphtho-quinone	C_2H_5OH	No reaction	(256)
3-Methyl-1-tetralone	Various alcohols	2-Hydroxy-3-methyl-1,2-naphthoquinone and 3-methyl-1,2-naphthoquinone	(256)
3-Ethyl-5-hydroxy-6,7-di-methoxy-1-tetralone	CH_3COOH or alcohol	Red dye formed	(253)
3-Ethyl-5,6,7-trimethoxy-1-tetralone	CH_3COOH or alcohol	No dye formation	(253)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
	4. Nitrogen compounds		
See table 1 for a list of amines and other nitrogen compounds that react with SeO_2 to form organic selenium compounds and table 2 for a number of nitrogen compounds used in qualitative tests for selenite			
Urea	C_2H_5OH and HCl	No reaction	(101)
Leucine	Sealed tube; 300°C.	Unidentified products	(261)
Diazoacetic ester	H_2SeO_3	Selenite reduced in aqueous solution	(126)
o-Aminophenol	Low temperature	Tarry resin	(54)
p-Aminophenol	Low temperature	Tarry resin	(54)
Pyridine (pure)	Reflux	No reaction	(95)
α-Picoline	Reflux	Picolinic acid and aldehyde	(95)
α-Picoline	$CH_3COOC_2H_5$	Picolinic acid and aldehyde (small yield)	(26)
β-Picoline	Reflux	Nicotinic acid	(95)
β-Picoline	H_2SO_4; 250–330°C.	Nicotinic acid; 50 per cent of theoretical	(259)
2,6-Lutidine		Dipicolinic acid	(95)
Quinoline (pure)	Reflux	No reaction	(95)
Quinoline	H_2SO_4; 250–330°C.	Nicotinic acid; 75 per cent of theoretical	(259)
Quinaldine	Xylene	α-Quinolinealdehyde and acid	(95)
Quinaldine	Xylene	α-Quinolinealdehyde and acid	(170)
Quinaldine	Aged H_2SeO_3	Quinaldoin	(125)
Lepidine	Aged H_2SeO_3	1,2-Di-4-quinolyl-ethylene	(125)
Lepidine	Xylene	Quinoline-4-aldehyde and cinchoninic acid	(130)
Lepidine		Quinoline-4-aldehyde (yield unsatisfactory)	(44)
6-Methoxylepidine	Xylene	6-Methoxyquinoline-4-aldehyde; 52 per cent yield	(130)
8-Nitrolepidine	C_2H_5OH	8-Nitroquinoline-4-aldehyde	(115)
8-Nitrolepidine		No reaction	(128)
2-Ethyl-3-methylquinoline		3-Methyl-2-carboxy-quinoline	(95)
2,3,8-Trimethylquinoline	C_2H_5OH	3,8-Dimethylquino-line-2-aldehyde	(31)
5-Nitro-2,3,8-trimethyl-quinoline	C_2H_5OH	5-Nitro-3,8-dimethyl-quinoline-2-aldehyde	(31)
1-Methylisoquinoline	Dioxane	Isoquinaldehyde; 42 per cent yield	(32)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
4. Nitrogen compounds—*Continued*			
1,3-Dimethyl-6,7-methylene dioxoisoquinoline	Dioxane	1,3-Dimethyl-6,7-methylenedioxoisoquinaldehyde	(32)
Acridine	300°C.; sealed tube	Dihydroacridine	(261)
9-Methylacridine	Sand bath	9-Acrinaldehyde	(171)
1,2,3,4-Tetrahydroacridine	$CH_3COOC_2H_5$	Acridine and 4-oxotetrahydroacridine	(26)
2-Methyl 3,4-tetrahydroacridine	$CH_3COOC_2H_5$	2-Methylacridine and 2-methyl-4-oxotetrahydroacridine	(26)
4-Hydroxy-2-methylquinazoline	CH_3COOH; 50–60°C.	4-Hydroxyquinazoline-2-aldehyde	(172)
2-Methyl-β-naphthoxazole	Toluene; 90°C.	β-Naphthoxazole-2-aldehyde	(110)
1,2-Dimethylbenzimidazole		1-Methylbenzimidazole 2-aldehyde	(110)
5,6-Benzo-7-azahydrindine		Benzoazahydrindone	(26)
Nicotine	H_2SO_4; 250–330°C.	Nicotinic acid; 75 per cent of theoretical	(259)
Hydroquinine	Xylene	Hydroquininone; 45 per cent yield	(140)
Papaverine	CH_3COOH	Papaveraldine	(160a)
Phenylsemicarbazide	H_2SeO_3	Qualitative test	(174)
Arylhydrazines	H_2SeO_3	Qualitative test	(70, 71, 90, 101, 174)
Hydrazones	H_2SeO_3	Qualitative test	(70)
Osazones	H_2SeO_3	Qualitative test	(70)
Phenylhydrazine	C_2H_5OH	Diphenylamine; 94 per cent yield	(188)
Phenylhydrazine	Acid solution	Tetraphenyltetrazene and blue dye	(188)
Phenylhydrazine hydrochloride	Acid solution	Product coupled with β-naphthol; 60 per cent dye	(188)
α-Naphthylhydrazine hydrochloride	Acid solution	Product coupled with β-naphthol; 25 per cent dye	(188)
β-Naphthylhydrazine hydrochloride	Acid solution	Product coupled with β-naphthol; 40 per cent dye	(188)

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
4. Nitrogen compounds—*Continued*			
m-Nitrophenylhydrazine hydrochloride	Acid solution	Product coupled with β-naphthol; 80 per cent dye	(188)
p-Nitrophenylhydrazine	Acid solution	*p*-Nitrophenyltriazine and $p\text{-}NO_2C_6H_4N{=}NNHC_6H_4NO_2\text{-}p$	(188)
5. Sulfur compounds			
See tables 1 and 2 for a list of sulfur compounds that react with selenium dioxide to form organic selenium compounds or are used in the qualitative analysis of selenite			
Thiocyanate ion	Acid solution	Se(s), CN^-, S^-, and H_2O	(136)
Thiocyanate ion	Acid solution	Se(s), NH_4^+, SO_4^{--}, S, and CO_2	(93)
Thiodiglycol	$CaCl_2$–SeO_2	Red selenium produced on moistening with water	(28)
β,β′-Dichlorodiethyl sulfide	$CaCl_2$–SeO_2	Red selenium produced on moistening with water	(28)
Phenylmercaptan	H_2SeO_3	Phenyl disulfide and organic selenium compounds	(101)
2-Hydroxythianaphthene	C_2H_5OH at 0°C.	Isothioindigo	(42a)
Thiourea	C_2H_5OH	Bis(aminoiminomethyl) disulfide	(254)
Substituted thioureas. Compounds giving test include methyl-, allyl-, diethyl-, trimethyl-, phenyl-, benzyldiethyl-, dimethylphenyl-thioureas; thioacetamide; and thiobenzamide. Tetrasubstituted thioureas do not react	C_2H_5OH	Qualitative test for —SH group in organic compounds	(255)
Substituted thioureas	H_2SeO_3	Qualitative test	(260)

Thioureas giving red color or precipitate: allyl-, di-*n*-butyl-, phenyl-, benzyl-, *o*-tolyl-, *p*-tolyl-, *p*-hydroxyphenyl-, *p*-fluorophenyl-, *p*-methoxyphenyl-, *p*-ethoxyphenyl-, *o*-*n*-butyloxyphenyl-, α-naphthyl-, di-*o*-hydroxycyclohexyl-, *N*-(β-hydroxyethyl)-*N*′-isoamyloxyphenyl-, *N*-methyl-*N*′-4-ethoxyphenyl-, and *N*-ethyl-*N*′-4-isobutyloxyphenyl-.

Thioureas giving pink color or precipitate: monolauryl-, *s*-diethyl-, 2,4-dimethylphenyl-, *ac*-tetrahydro-β-naphthyl-, phenylethanol-, *s*-di-*o*-tolyl-, *N*-4-ethoxyphenylpiperidyl-, *N*-(β-hydroxyethyl)-*N*′-4-allyloxyphenyl-, *N*-dimethyl-*N*′-4-ethoxyphenyl-, and *N*-(*n*-butyl)-*N*′-4-ethoxyphenyl-.

Thioureas giving yellow color or precipitate: *m*-tolyl-, xylidyl-, *s*-diphenyl-, *s*-di-*m*-tolyl-, phenyl-*o*-tolyl-, *p*-isoamyloxyphenyl-, dimethylcyclohexyl-, *N*-dimethyl-*N*′-4-isopropyloxyphenyl-, *N*-(di-*n*-butyl)-*N*′-4-ethoxyphenyl-, *N*-(*p*-chlorophenyl)-*N*′-acetyl, and *N*,*N*′-di(*p*-hydroxyphenyl)-; also *m*-phenylene- and *p*-phenylene-dithioureas.

TABLE 3—*Continued*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
6. Oxidations with SeO_2 in concentrated sulfuric acid			
Many organic compounds react with selenium dioxide to form organic selenium compounds, as shown in table 1; reactions of analytical interest are listed in table 2			
Carbon monoxide	Effect of catalysts and temperature on the oxidation to CO_2		(165–167)
Carbon oxysulfide	Effect of catalysts and temperature on the oxidation to CO_2		(166)
Ethylene	Effect of catalysts and temperature on the oxidation to CO_2		(166)
Sucrose	Effect of catalysts and temperature on the oxidation to CO_2		(166)
Diphenylamine	SeO_2–H_2SO_4	Cornflower-blue color	(137)
Pyrrole	SeO_2–H_2SO_4	Blue color	(20, 213)
Codeine	SeO_2–H_2SO_4	Blue-green color	(109)
Codeine phosphate	SeO_2–H_2SO_4	Blue-green color	(192)
Aspidospermine	SeO_2–H_2SO_4	Blue-green color	(184)
Alkaloids	SeO_2–H_2SO_4	Color reactions	(30, 57, 73, 109, 118, 131, 133, 149, 151, 181a, 184, 217)
β-Picoline	SeO_2–H_2SO_4	See Section 4 (oxidation of nitrogen compounds)	
Quinoline	SeO_2–H_2SO_4	See Section 4 (oxidation of nitrogen compounds)	
Nicotine	SeO_2–H_2SO_4	See Section 4 (oxidation of nitrogen compounds)	
Nitrogen compounds	SeO_2–H_2SO_4	Color reactions	(55)

Compounds that produce colors are: *o*-aminodiphenyl, *p*-aminodiphenyl, 4-aminodiphenylamine, benzeneazodiphenylamine, aniline, *p*-bromoaniline, *m*-chloroaniline, carbanilide, diphenylamine, 2,4-diaminodiphenylamine, dibenzylaniline, di-2-naphthylamine, diphenylbenzidine, formyldiphenylamine, methyldiphenylamine, 4-nitrodiphenylamine, *o*-toluidine hydrochloride, *p*-toluidine hydrochloride, tolidine, 1-naphthylamine, 2-naphthylamine, *s*-diphenylethylenediamine, *s*-dimethylcarbanilide, diphenylcarbamine hydrochloride, *s*-diphenylcarbazide, *s*-diphenylcarbazone, 4,5-diphenylglyoxalone, diphenylpiperazine, 1,4-diphenylsemicarbazide, 4,4-diphenylsemicarbazide, *p*-nitrophenylhydrazine, *l*-leucine, cholesterol, carbanilide, tryptophan, triphenylguanidine, cysteine hydrochloride, di-*p*-phenetylurea, *s*-di-*o*-tolylurea, *s*-di-*m*-tolylurea, *s*-di-*p*-tolylurea, *s*-di-*o*-tolylthiourea, *s*-di-*p*-tolylthiourea, phenylthiourea, thiocarbanilide, methylthiocarbanilide, and diphenylthiocarbazide.

Compounds giving either a faint pink or no color at all: ethylamine hydrobromide, ethylenediamine, 2-propanolamine, triethanolamine, tri-2-propanolamine, morpholine, hexamethyleneamine, dimethylaniline, diethylaniline, *o*-chloroaniline, *p*-chloroaniline,

TABLE 3—*Concluded*

NAME OF COMPOUND OXIDIZED	REACTION CONDITIONS	PRODUCTS FORMED	REFERENCES
6. Oxidations with SeO_2 in concentrated sulfuric acid—*Continued*			
methylaniline, *n*-nitroaniline, tribenzylamine, hydroxylamine hydrochloride, guanidine hydrochloride, diphenylguanidine, di-*o*-tolylguanidine, *o*-, *m*-, and *p*-aminobenzoic acids, *p*-dimethylaminobenzaldehyde, sulfanilic acid, urea, phenylurea, *s*-diethylcarbanilide, thiourea, allylthiourea, phenylhydrazine, pyridine, α-picoline, quinoline, glycine, *l*-cystine, *dl*-α-amino-α-methylbutyric acid, *l*-proline, *l*-oxyproline, *dl*-serine, *dl*-valine, *dl*-isoleucine, asparagine, creatinine, *d*-arginine hydrochloride, β-phenylalanine, diiodotyrosine, barbituric acid, and phenobarbital. *Compounds giving same color as in concentrated sulfuric acid alone:* methyl-*o*-, methyl-*m*-, and methyl-*p*-toluidines, dibenzylamine, *o*- and *m*-bromoanilines, *p*-nitroaniline, *m*- and *p*-phenylenediamines, benzidine, *p*,*p*′-diaminodiphenylmethane, *p*-nitrosodiphenylamine, diphenylnitrosamine, and diphenylthiocarbazone.		
Phenolic compounds.....	SeO_2–H_2SO_4	Color reactions	(134)
The following compounds were tested: phenol, amidol, anisole, phenetole, phenacetin, acetylsalicyclic acid, cresols, salicylaldehyde, methyl and phenyl salicylates, pyrocatechol, guaiacol, vanillin, vanillic acid, piperonol, resorcinol, hydroquinone, pyrogallol, phloroglucinol, eugenol, thymol, carvacrol, α and β- naphthols, chrysarobin; the glucosides arbutin and phloridzin; the alkaloids morphine, heroin, dionine, narcotine, narceine, and papaverine; the dyes orcein, alizarin, and purpurin. Mono-, di-, and trinitrophenols do not produce colors; phenolic aldehydes and acids give only faint colors. Cholesterol plus acetic anhydride in SeO_2–H_2SO_4 yields a fleeting purple going over to red.			

VII. REFERENCES

(1) ADAMS, D. F., AND GILBERTSON, L. I.: Ind. Chem. Eng., Anal. Ed. **14**, 926 (1942).
(2) ALDER, K., AND STEIN, G.: Ann. **504**, 205 (1933).
(3) ALLARD, J.: Bull. inst. pin. **2**, 727 (1934).
(4) ARMSTRONG, K. F., AND ROBINSON, R.: J. Chem. Soc. **1934**, 1650.
(5) ASAHIMA, Y., ISHIDATE, M., AND MOMOSE, T.: Ber. **67**, 1432 (1934).
(6) ASTIN, S., MOULDS, L. DE V., AND RILEY, H. L.: J. Chem. Soc. **1935**, 901.
(7) ASTIN, S., NEWMAN, A. C. C., AND RILEY, R. L.: J. Chem. Soc. **1933**, 391.
(8) ASTIN, S., AND RILEY, H. L.: J. Chem. Soc. **1934**, 833.
(9) BACKER, H. J., AND STRATING, J.: Rec. trav. chim. **53**, 1113 (1934).
(10) BADGER, G. M.: J. Chem. Soc. **1941**, 535.
(11) BAKER, R. H., AND MAXSON, R. N.: *Inorganic Syntheses*, Vol. 1, p. 119. John Wiley and Sons, Inc., New York (1939).
(12) BARBIER, H.: Helv. Chim. Acta **23**, 531, 1477 (1940).
(13) BARNES, E.: J. Indian Chem. Soc. **9**, 329 (1932).
(14) BARNES, E.: J. Indian Chem. Soc. **12**, 22 (1935).
(15) BATTEGAY, M., AND HUGEL, G.: Bull. soc. chim. **27**, 557 (1920).
(16) BATTEGAY, M., AND HUGEL, G.: Bull. soc. chim. **31**, 440 (1922).
(17) BATTEGAY, M., AND HUGEL, G.: Bull. soc. chim. **33**, 1103 (1923).
(18) BATTEGAY, M., AND VECHOT, J.: Bull. soc. chim. **37**, 1271 (1925).
(19) BELLAMY, L. J., AND DOREE, C.: J. Chem. Soc. **1941**, 176.
(20) BERG, R., AND TEITELBAUM, M.: Mikrochemie, Emich Festschrift, p. 23 (1930).
(21) BERGMANN, W., AND KIND, C. A.: J. Am. Chem. Soc. **64**, 473 (1942).
(21a) BERGSTROM, F. W.: Chem. Rev. **35**, 120, 186 (1944).
(21b) BERSIN, T.: Ergeb. Enzymforsch. **4**, 68 (1935).

(22) BILHAM, P., KON, G. A. R., AND ROSS, W. C. J.: J. Chem. Soc. **1942**, 535.
(23) BIRD, M. L., AND CHALLENGER, F.: J. Chem. Soc. **1939**, 163.
(24) BLACET, F. E., AND MOULTON, R. W.: J. Am. Chem. Soc. **63**, 868 (1941).
(25) BORGWARDT, E., AND SCHWENK, E.: J. Am. Chem. Soc. **56**, 1185 (1934).
(26) BORSCHE, W., AND HARTMANN, H.: Ber. **73B**, 839 (1940).
(27) BORSOOK, H., ELLIS, E. L., AND HUFFMAN, H. M.: J. Biol. Chem. **117**, 281 (1937).
(28) BRADLEY, T. F.: Chem. Eng. News **20**, 893 (1942).
(29) BRADSTREET, R. B.: Chem. Rev. **27**, 331 (1940).
(30) BRANDT, C.: Jahresber. Pharm., p. 341 (1875).
(31) BURGER, A., AND MODLIN, L. R., JR.: J. Am. Chem. Soc. **62**, 1081 (1940).
(32) BURROWS, R. S., AND LINDWALL, H. G.: J. Am. Chem. Soc. **64**, 2430 (1942).
(33) BUTENANDT, A., AND HAUSMANN, E.: Ber. **70**, 1154 (1937).
(34) CALLOW, R. K.: J. Chem. Soc. **1936**, 462.
(35) CALLOW, R. K., AND ROSENHEIM, O.: J. Chem. Soc. **1933**, 387.
(36) CALVIN, M., AND WOOD, C. L.: J. Am. Chem. Soc. **62**, 3152 (1940).
(37) CAMPBELL, W. P., AND HARRIS, G. C.: J. Am. Chem. Soc. **63**, 2721 (1941); **64**, 720 (1942).
(38) CARNEVALI, F.: Atti accad. Lincei [5] **17**, ii, 385 (1908).
(39) CARTER, S. R., BUTLER, J. A. V., AND JAMES, F.: J. Chem. Soc. **1926**, 930.
(40) CHABRIE, C.: Bull. soc. chim. [3] **2**, 788 (1889).
(41) CHAKRAVARTI, S. M., AND SWAMINATHAN, M.: Current Sci. **2**, 472 (1934).
(42) CHERNYI, M. E.: Trudy i Materialy Sverdlov. Inst. Eksptl. Med. **1940**, No. 4, 175.
(42a) CHOVIN, P.: Compt. rend. **215**, 419 (1942).
(43) CLARK, C. W. (to Canadian Copper Refiners Ltd.): U. S. patent 2,322,348 (June, 1943).
(44) CLEMO, G. R., AND HOGGARTH, E.: J. Chem. Soc. **1939**, 1241.
(45) DE CONINCK, W. O.: Compt. rend. **142**, 571 (1906).
(46) DE CONINCK, W. O., AND CHAUVENET, E.: Bull. acad. roy. Belg. **1906**, 51.
(47) DE CONINCK, W. O., AND CHAUVENET, E.: Bull. acad. roy. Belg. **1906**, 601.
(48) CONNOR, R., FLEMING, C. L., JR., AND CLAYTON, T.: J. Am. Chem. Soc. **58**, 1386 (1936).
(49) COOK, J. W.: J. Chem. Soc. **1932**, 1472.
(50) COPP, F. C., AND SIMONSEN, J. L.: J. Chem. Soc. **1942**, 209.
(51) CROWELL, J. H., AND BRADT, W. E.: J. Am. Chem. Soc. **55**, 1500 (1933).
(52) CURTIS, H. A., AND BURNS, R. M.: J. Am. Chem. Soc. **39**, 33 (1917).
(53) DANE, E., SCHMITT, J., AND RAUTENSTRAUCH, C.: Ann. **532**, 29 (1937).
(54) DEUPREE, J. F., AND LYONS, R. E.: Proc. Indiana Acad. Sci. **46**, 101 (1937).
(55) DEWEY, B. T., AND GELMAN, A. H.: Ind. Eng. Chem., Anal. Ed. **14**, 361 (1942).
(56) DOREE, C., AND PETROW, V. A.: J. Chem. Soc. **1935**, 1391.
(57) DRAGENDORFF, J. G.: Z. Chem. [2] **2**, 3 (1866).
(58) DREYFUS, H.: French patent 770,420 (September, 1934).
(59) DUPONT, G., ALLARD, J., AND DULOU, R.: Bull. soc. chim. **53**, 599 (1933).
(60) DUPONT, G., AND ZACHAREWICZ, W.: Compt. rend. **200**, 759 (1935).
(61) DUPONT, G., ZACHAREWICZ, W., AND DULOU, R.: Compt. rend. **198**, 1699 (1934).
(62) DUPONT, R.: Ind. chim. belge **10**, 307 (1939).
(63) ECK, J. C., AND HOLLINGSWORTH, E. W.: J. Am. Chem. Soc. **64**, 140 (1942).
(64) EMELEUS, H. J., AND RILEY, H. L.: Proc. Roy. Soc. (London) **A140**, 378 (1933).
(65) EVANS, W. C., RIDGEON, J. M., AND SIMONSEN, J. L.: J. Chem. Soc. **1934**, 137.
(66) FALCIOLA, P.: Ann. chim. applicata **17**, 261 (1927).
(67) FARBWERKE VORM. M. L. G. B.: German patent 299,510 (1917).
(68) FARBWERKE VORM. M. L. G. B.: German patents 348,906 and 350,376 (1918).
(69) FARMER, E. H.: Trans. Faraday Soc. **38**, 347 (1942); J. Chem. Soc. **1942**, 124.
(69a) FEIGL, F.: J. Chem. Education **22**, 36 (1945).
(70) FEIGL, F., AND DEMANT, V.: Mikrochim. Acta **1**, 134 (1937). *Cf.* FEIGL, F., AND DEMANT, V.: *Spot Tests*, pp. 321–5. Nordemann Publishing Company, Inc., New York (1943).

(71) FEIGL, F., AND DEMANT, V.: Mikrochim. Acta **1**, 322 (1937).
(72) FEIGL, F., AND FEIGL, E.: Z. anorg. allgem. Chem. **20**, 357 (1931).
(73) FERREIRA DA SILVA, A. J.: Compt. rend. **112**, 1266 (1891).
(74) FIRTH, J. B., AND GETHING, H. H.: J. Chem. Soc. **1936**, 633.
(75) FISCHER, E. (to Bayer and Co.): U. S. patent 1,074,425 (September, 1913); Swiss patent 62,686 (February, 1913).
(76) FISHER, C. H.: J. Am. Chem. Soc. **56**, 2056 (1934).
(77) FISHER, C. H., AND EISNER, A. J.: J. Org. Chem. **6**, 169 (1941).
(78) FOKIN, S. A.: J. Russ. Phys. Chem. Soc. **45**, 285 (1913).
(79) FUSON, R. C., ARMSTRONG, M. D., WALLACE, W. E., AND KNEISLEY, J. W.: J. Am. Chem. Soc. **66**, 1274 (1944).
(80) FUSON, R. C., GRAY, H., AND GOUZA, J. J.: J. Am. Chem. Soc. **61**, 1937 (1939).
(81) FUSON, R. C., MATUSZESKI, J. F., AND GRAY, A. R.: J. Am. Chem. Soc. **56**, 2100 (1934).
(81a) FUSON, R. C., AND SOPER, A. F.: J. Org. Chem. **9**, 193 (1944).
(82) FUSON, R. C., SOUTHWICK, P. L., AND ROWLAND, S. P.: J. Am. Chem. Soc. **66**, 1109 (1944).
(83) GASSMANN, T.: Z. physiol. Chem. **100**, 209 (1917).
(84) GEILMANN, W., AND WRIGGE, F. W.: Z. anorg. allgem. Chem. **210**, 357 (1933).
(85) GODCHOT, M., AND CAUQUIL, G.: Compt. rend. **202**, 326,444 (1936).
(86) GRAY, A. R., AND FUSON, R. C.: J. Am. Chem. Soc. **56**, 739 (1934).
(87) GUILLEMONAT, A.: Compt. rend. **201**, 904 (1935).
(88) GUILLEMONAT, A.: Compt. rend. **200**, 1416 (1935).
(89) GUILLEMONAT, A.: Ann. chim. **11**, 143 (1939).
(90) GUTBIER, A.: Z. anorg. Chem. **32**, 257 (1902).
(91) HAGISAWA, H.: Bull. Inst. Phys. Chem. Research (Tokyo) **18**, 648 (1939).
(92) HAHN, G., AND SCHALES, O.: Ber. **67**, 1823 (1934).
(93) HALL, W. T.: Ind. Eng. Chem., Anal. Ed. **10**, 395 (1938).
(93a) HATT, H. H., PILGRIM, A., AND HURRAN, W. J.: J. Chem. Soc. **1936**, 93.
(94) HEINEMANN, F.: German patent 261,412 (February, 1912); British patent 3042 (February, 1913).
(95) HENZE, M.: Ber. **67**, 750 (1937).
(96) HENZE, M., AND HENZE, C.: German patent 697,759 (September, 1940).
(97) HILDITCH, T. P., AND SMILES, S.: J. Chem. Soc. **93**, 1384 (1908).
(98) HILL, A. E., SOTH, G. C., AND RICCI, J. E.: J. Am. Chem. Soc. **62**, 2719 (1940).
(99) HINSBERG, O.: Ber. **22**, 863, 866, 2897 (1889).
(100) HINSBERG, O.: Ber. **23**, 1393 (1890).
(101) HINSBERG, O.: Ann. **260**, 40 (1890); Ber. **24**, 5 (1891).
(102) HINSBERG, O.: Ber. **52B**, 21 (1919).
(103) HIRAYAMA, S.: J. Chem. Soc. Japan **58**, 1393 (1937).
(104) HIRAYAMA, S.: J. Chem. Soc. Japan **59**, 67 (1938).
(105) HIRAYAMA, S.: J. Chem. Soc. Japan **59**, 229 (1938).
(106) HIRAYAMA, S.: J. Chem. Soc. Japan **59**, 683 (1938).
(107) HIRAYAMA, S.: Chem. Rev. (Japan) **5**, 134 (1939).
(108) HOLWEG, W., AND HERLOFF, H. (to Schering A.-G.): German patent 705,862 (April, 1941).
(109) HORN, M. L.: Ind. Eng. Chem., Anal. Ed. **6**, 34 (1934).
(110) I. G. Farbenindustrie A.-G.: French patent 847,527 (October, 1939).
(111) I. G. Farbenindustrie A.-G.: French patent 842,509 (June, 1939).
(112) ISHIKAWA, F., AND ABE, H.: Sci. Papers Inst. Phys. Chem. Research (Tokyo) **34**, 775 (1938).
(113) ISIDATE, M., KAWAKATA, H., AND MAKAGAWA, K.: Ber. **74B**, 1707 (1941).
(114) IVANOV, W. N.: Chem.-Ztg. **32**, 468 (1908).
(115) JOHNSON, O. H., AND HAMILTON, C. S.: J. Am. Chem. Soc. **63**, 2864 (1941).
(116) JONES, E. R. H., AND MEAKINS, R. J.: J. Chem. Soc. **1941**, 757.
(117) JOSHEL, L. M., AND PALKIN, S.: J. Am. Chem. Soc. **64**, 1008 (1942).

(118) JOUVE, A.: Bull. soc. chim. [3] **25**, 489 (1901).
(119) JULIEN, A. P.: Bull. soc. chim. **47**, 1799 (1925).
(120) JUNG, W.: Anales soc. cient. argentina **132**, 201 (1941).
(121) KACER, K. (to I. G. Farbeindustrie A.-G.): German patent 557,249 (December, 1929).
(122) KACER, K. (to I. G. Farbenindustrie A.-G.): British patent 347,743 (October, 1930).
(123) KACER, K. (to General Aniline Works, Inc.): U. S. patent 1,935,949 (November, 1933).
(124) KAMECKI, J.: Roczniki Chem. **19**, 433 (1939).
(125) KAPLAN, H.: J. Am. Chem. Soc. **63**, 2654 (1941).
(126) KARVE, D. D.: J. Indian Chem. Soc. **2**, 128 (1925).
(127) KAUTTER, C. T. (to Röhm and Haas Co.): U. S. patent 2,171,727 (September, 1939).
(128) KRAHLER, S. E., AND BURGER, A.: J. Am. Chem. Soc. **64**, 2417 (1942).
(129) KRATZL, K.: Österr. Chem. Ztg. **41**, 340 (1938).
(130) KWARTLER, C. E., AND LINDWALL, H. G.: J. Am. Chem. Soc. **59**, 524 (1937).
(131) LAFON, P.: Compt. rend. **100**, 1543 (1885).
(132) LATIMER, W. M.: *Oxidation Potentials*, pp. 64–81. Prentice-Hall, Inc., New York (1938).
(133) LAURO, M. F.: Ind. Eng. Chem., Anal. Ed. **3**, 401 (1931).
(134) LEVINE, V. E.: J. Lab. Clin. Med. **11**, 809 (1926); Science [2] **52**, 207 (1920).
(135) LINSTEAD, R. P.: Annual Reports of the Chemical Society **34**, 238 (1937).
(136) LJUNG, H. A.: Ind. Eng. Chem., Anal. Ed. **9**, 328 (1937); J. Elisha Mitchell Sci. Soc. **53**, 229 (1937).
(136a) LOMBARD, R.: Compt. rend. **213**, 793 (1941); Fette u. Seifen **50**, 377 (1943).
(137) LUNGE, G.: Ber. **20**, 2032 (1887).
(138) LU VALLE, J. E., AND SCHOMAKER, V.: J. Am. Chem. Soc. **61**, 3521 (1939).
(139) LYONS, R. E., AND BRADT, W. E.: Ber. **60**, 60 (1927).
(140) MCKEE, R. L., AND HENZE, H. R.: J. Am. Chem. Soc. **66**, 2022 (1944).
(141) MARINO, L., AND SQUINTANI, V.: Atti accad. Lincei **20**, II, 666 (1911).
(142) MARINO, L., AND TONINELLI, A.: Atti accad. Lincei **21**, II, 98 (1912).
(143) MARKER, R. E. (to Parke Davis and Co.): U. S. patent 2,352,849 (July, 1944).
(144) MARKER, R. E., CROOKS, H. M., AND WITTBECKER, E. L.: J. Am. Chem. Soc. **63**, 777 (1941).
(145) MARKER, R. E., KAMM, O., AND WITTLE, E. L. J. Am. Chem. Soc. **60**, 1071 (1938).
(146) MARKER, R. E., AND ROHRMANN, E.: J. Am. Chem. Soc. **60**, 1073 (1938).
(147) MARKER, R. E., AND TURNER, D. L.: J. Am. Chem. Soc. **63**, 769 (1941).
(148) MARTIN, R. H., AND ROBINSON, R.: J. Chem. Soc. **1943**, 491.
(149) MARTINI, A.: Univ. nacl. litoral (Rosario, Argentina) **3**, 5 (1939).
(150) MAYOR, Y.: Chimie & industrie **43**, 188 (1940).
(151) MECKE, P.: Z. öffentl. Chem. **5**, 351 (1899).
(152) MELNIKOV, N. N.: Uspekhi Khim. **5**, 443 (1936).
(153) MELNIKOV, N. N., AND ROKITSKAYA, M. S.: J. Gen. Chem. (U.S.S.R.) **7**, 1532 (1937).
(154) MELNIKOV, N. N., AND ROKITSKAYA, M. S.: J. Gen. Chem. (U.S.S.R.) **7**, 2738 (1937).
(155) MELNIKOV, N. N. AND ROKITSKAYA, M. S.: J. Gen. Chem. (U.S.S.R.) **8**, 834 (1938).
(156) MELNIKOV, N. N., AND ROKITSKAYA, M. S.: J. Gen. Chem. (U.S.S.R.) **8**, 1369 (1938).
(157) MELNIKOV, N. N., AND ROKITSKAYA, M. S.: J. Gen. Chem. (U.S.S.R.) **9**, 1158 (1939).
(158) MELNIKOV, N. N., AND ROKITSKAYA, M. S.: J. Gen. Chem. (US.S.R.) **9**, 1808 (1939).
(159) MELNIKOV, N. N., AND ROKITSKAYA, M. S.: J. Gen. Chem. (U.S.S.R.) **10**, 1439 (1940).
(160) MELNIKOV, N. N., AND ROKITSKAYA, M. S.: J. Gen. Chem. (U.S.S.R.) **10**, 1713 (1940).
(160a) MENON, K. N.: Proc. Indian Acad. Sci. **19A**, 21 (1944).
(161) MEYER, JL.: Ber. **55B**, 2082 (1922).
(162) MEYER, JL., AND JANNEK, J.: Z. anorg. Chem. **83**, 62 (1913).
(163) MICHAELIS, A., AND LANDMANN, B.: Z. anorg. Chem. **13**, 656 (1880).
(164) MIESCHER, K., AND WETTSTEIN, A. (to Ciba Co.): U. S. patents 2,323,276 and 2,323,277 (June, 1944).
(165) MILBAUER, J.: Z. Elektrochem. **41**, 594 (1935); *cf.* Chem Obzor. **11**, 208 (1936); **12**, 17 (1937); **16**, 97 (1941).

(166) MILBAUER, J.: Chem. Obzor. **11**, 1, 65, 132, 183, 233 (1936).
(167) MILBAUER, J.: Chem. Obzor. **14**, 233 (1939); **16**, 1 (1941).
(168) MILBAUER, J.: Chem. Obzor. **15**, 145 (1940).
(169) MILBAUER, J., AND MIKOLASEK, J.: Chem. Obzor. **15**, 65, 84 (1940).
(170) MONTI, L.: Atti accad. Lincei **18**, 505 (1933).
(171) MONTI, L.: Atti accad. Lincei **24**, 145 (1936).
(172) MONTI, L.: Atti accad. Lincei **28**, 96 (1938).
(173) MONTI, L.: Atti X° congr. intern. chim. **3**, 256 (1939).
(174) MONTIGNIE, E.: Bull. soc. chim. **51**, 127 (1932).
(175) MONTIGNIE, E.: Bull. soc. chim. [5] **1**, 290 (1934).
(176) MOWER, M., GREEN, J., AND SPRING, F. S.: J. Chem. Soc. **1944**, 256.
(177) MÜLLER, R.: Ber. **66B**, 1668 (1933).
(178) NAESER, C. R.: *Inorganic Syntheses*, Vol. 1, p. 117. John Wiley and Sons, Inc., New York (1939).
(179) NAMETKIN, S. S., AND SHEREMAT'EVA, T. V.: Compt. rend. acad. sci. U.R.S.S. **38**, 131 (1943).
(180) NAVES, Y. R., AND IGOLEN, M. G.: Bull. inst. pin. **1935**, 234.
(181) OLSON, O. E., AND JENSEN, C. W.: Proc. S. Dakota Acad. Sci. **20**, 115 (1940).
(181a) ORLOFF, N. A.: Chem.-Ztg. **25**, 66 (1901).
(182) PAILLARD, H., AND SZASZ, R.: Helv. Chim. Acta **26**, 1856 (1943).
(183) PAINTER, E. P.: Chem. Rev. **28**, 179 (1941).
(184) PALET, L. P. J.: Ann. chim. anal. **23**, 25 (1918).
(185) PICARD, C. W. AND SPRING, F. S.: J. Chem. Soc. **1941**, 35.
(186) PIUTTI, P.: Gazz. chim. ital. **66**, 276 (1936).
(187) POSTOVSKII, J. YA., AND LUGOVKIN, B. P.: Ber. **68B**, 852 (1935).
(188) POSTOVSKII, J. YA., LUGOVKIN, B. P., AND MANDRYK, G. T.: Ber. **69B**, 1913 (1936).
(189) PRASAD, M., AND DHARMATTI, S. S.: Proc. Indian Acad. Sci. **12A**, 185 (1940).
(190) PRIDEAUX, E. B. R., AND GREEN, G.: J. Phys. Chem. **28**, 1273 (1924).
(191) PRINGLE, P.: Brit. J. Dermatol. Syphilis **54**, 54 (1942).
(192) RAIKHINSTEIN, TZ.: Trans. Inst. Pure Chem. Reagents (U.S.S.R.) **6**, 27 (1927).
(193) RAPPEN, L.: J. prakt. Chem. **157**, 177 (1941).
(194) RILEY, H. L. (to Imperial Chemical Industries Ltd.): British patent 354,798 (February, 1930).
(195) RILEY, H. L. (to Imperial Chemical Industries Ltd.): British patent 376,306 (July, 1932).
(196) RILEY, H. L. (to Imperial Chemical Industries Ltd.): U. S. patent 1,955,890 (April, 1934).
(197) RILEY, H. L. (to Imperial Chemical Industries Ltd.): U. S. patent 1,999,576 (April, (1935).
(198) RILEY, H. L., AND FRIEND, N. A. C.: J. Chem. Soc. **1932**, 2342.
(199) RILEY, H. L., AND GRAY, A. R.: *Organic Syntheses*, Vol. 15, p. 67. John Wiley and Sons, Inc., New York (1935).
(200) RILEY, H. L., MORLEY, J. F., AND FRIEND, N. A. C.: J. Chem. Soc. **1932**, 1876.
(201) RONZIO, A. R., AND WAUGH, T. D.: *Organic Syntheses*, Vol. 24, p. 61. John Wiley and Sons, Inc., New York (1944).
(202) ROSENHEIM, O., AND STARLING, W. W.: J. Chem. Soc. **1937**, 377.
(203) RUSSELL, W. F. (to R. T. Vanderbilt Co., Inc.): U. S. patent 2,347,128 (April, 1944).
(204) RUZICKA, L., AND BERNOLD, E.: Helv. Chim. Acta **24**, 1167 (1941).
(205) RUZICKA, L., BRENNER, M., AND REY, E.: Helv. Chim. Acta **25**, 161 (1942).
(206) RUZICKA, L., AND JEGER, O.: Helv. Chim. Acta **24**, 1178 (1941).
(207) RUZICKA, L., AND JEGER, O.: Helv. Chim. Acta **25**, 775 (1942).
(208) RUZICKA, L., JEGER, O., AND NORYMBERSKI, J.: Helv. Chim. Acta **25**, 457 (1942).
(209) RUZICKA, L., AND PLATTNER, PL. A.: Helv. Chim. Acta **20**, 809 (1937).
(210) RUZICKA, L., PLATTNER, PL. A., AND PATAKI, J.: Helv. Chim. Acta **25**, 425 (1942).
(211) RUZICKA, L., AND ROSENKRANZ, G.: Helv. Chim. Acta **23**, 2311 (1940).

(212) SA, A.: Rev. centro estud. farm. bioquím. **27**, 19, 48 (1937).
(213) SACCARDI, P., AND MARTINI, G.: Chim. ind. agr. biol. **13**, 210 (1937).
(214) SACHS, F.: Ann. **365**, 150 (1909).
(215) SACHS, F., AND MEYERHEIM, G.: Ber. **41**, 3957 (1908).
(216) SADOVSKII, P. I.: Zavodskaya Lab. **8**, No. 10–11, 1184 (1939).
(217) SCHMIDT, E.: Arch. Pharm. **252**, 161 (1914).
(218) SCHMITT, J.: Ann. **547**, 103 (1941).
(219) SCHOTT, H. F., SWIFT, E. H., AND YOST, D. M.: J. Am. Chem. Soc. **50**, 721 (1928).
(220) SCHWENK, E., AND BORGWARDT, E.: Ber. **65B**, 1601 (1932).
(221) SCHWENK, E., AND BORGWARDT, E. (to Schering-Kahlbaum A.-G.): German patent 582,545 (August, 1933).
(222) SCHWENK, E., AND BORGWARDT, E. (to Schering-Kahlbaum A.-G.): British patent 403,838 (1933).
(223) SCHWENK, E., AND BORGWARDT, E. (to Schering-Kahlbaum A.-G.): French patent 751,807 (September, 1933).
(224) SCHWENK, E., AND BORGWARDT, E. (to Schering-Kahlbaum A.-G.): German patent 584,373 (September, 1933).
(225) SEGUIN, P.: Compt. rend. **216**, 667 (1943).
(225a) SERGEEFF, M. P.: Russ. Pharm. J. **36**, 431 (1897).
(226) SILVERTHORN, R. W.: Chemist-Analyst **30**, 52, 62 (1941).
(227) SOCIÉTÉ POUR L'INDUSTRIE CHIMIQUE À BÂLE: Swiss patents 212,336 and 212,337 (March, 1941).
(228) SOCIÉTÉ POUR L'INDUSTRIE CHIMIQUE À BÂLE: British patent 550,683 (January, 1943).
(229) SREENIVASAN, A., AND SADISIVAN, V.: Ind. Eng. Chem., Anal. Ed. **11**, 314 (1939).
(230) STALLCUP, W. D., AND HAWKINS, J. E.: J. Am. Chem. Soc. **63**, 3339 (1941).
(231) STALLCUP, W. D., AND HAWKINS, J. E.: J. Am. Chem. Soc. **64**, 1807 (1942).
(232) STAMM, H., AND GOSSRAU, K.: Ber. **66B**, 1558 (1933).
(233) STEIN, G.: Angew. Chem. **54**, 146 (1941).
(234) STEKOL, J. A.: J. Am. Chem. Soc. **64**, 1742 (1942).
(235) STILLER, E. T., AND ROSENHEIM, O.: J. Chem. Soc. **1938**, 353.
(236) STOLBA, F.: Z. anal. Chem. **11**, 437 (1872).
(237) SWAIN, G., AND TODD, A. R.: J. Chem. Soc. **1942**, 626.
(238) TABOURY, M. F., AND QUEUILLE, J.: Compt. rend. **217**, 150 (1943).
(239) TABUTEAU, J.: Compt. rend. **200**, 244 (1935).
(240) TAKAMATSU, M.: J. Pharm. Soc. (Japan) **48**, 450 (1928).
(240a) TEETERS, W. O., AND SHRINER, R. L.: J. Am. Chem. Soc. **55**, 3026 (1933).
(241) TREADWELL, W. D., AND FRÄNKEL, E.: German patent 279,005 (December, 1913).
(242) TRUCHET, R.: Compt. rend. **196**, 706 (1933).
(243) TRUCHET, R.: Compt. rend. **196**, 1613 (1933).
(244) TSCHUGAJEW, L., AND CHLOPIN, W.: Ber. **47**, 1269 (1914).
(245) TURK, A., DAWSON, J. W., AND SOLOWAY, S.: Am. Paint J. **28**, 16, 18, 20 (1943).
(246) URBAN, G.: Arch. exptl. Path. Pharmakol. **202**, 337 (1943).
(247) URION, E.: Compt. rend. **199**, 363 (1934).
(248) VENE, J.: Compt. rend. **216**, 772 (1943).
(249) VEREINIGTE CHININFABRIKEN ZIMMER & CIE, G. M. B. H.: German patent 331,145 (December, 1920).
(250) WAGENMAN, K. (to Mansfeldscher Kupferschieferbergbau A.-G.): German patent 700,497 (November, 1940).
(251) WAITKINS, G. R.: Unpublished observations.
(252) WAITKINS, G. R., BEARSE, A. E., AND SHUTT, R.: Ind. Eng. Chem. **34**, 899 (1942).
(253) WALLENFELS, K.: Ber. **74B**, 1428 (1941).
(254) WERNER, A. E. A.: Analyst **65**, 286 (1940).
(255) WERNER, A. E. A.: Sci. Proc. Roy. Dublin Soc. **22**, 387 (1941).

(255a) WEYGAND, C.: Beiheft Z. Ver. Deut. Chem. No. **45**; Die Chemie **55**, 60 (1942).
(256) WEYGAND, F., AND SCHRÖDER, K.: Ber. **74B**, 1844 (1941).
(257) WIERZCHOWSKI, P.: Roczniki Chem. **16**, 451 (1936).
(258) WOLFRAM, M. L., AND MAHAN, J.: J. Am. Chem. Soc. **64**, 311 (1942).
(259) WOODWARD, C. F., BADGETT, C. O., AND KAUFMAN, J. G.: Ind. Eng. Chem. **36**, 544 (1944).
(260) YOE, J. H., AND OVERHOLSER, L. G.: Ind. Eng. Chem., Anal. Ed. **14**, 435 (1942).
(261) YOKOYAMA, M.: J. Chem. Soc. Japan **59**, 262, 271 (1938).
(262) YOST, D. M., AND HATCHER, J. B.: J. Am. Chem. Soc. **54**, 151 (1932).
(263) YOST, D. M., AND RUSSELL, H., JR.: *Systematic Inorganic Chemistry*, pp. 318, 345. Prentice-Hall, Inc., New York (1944).
(264) ZACHAREWICZ, W.: Roczniki Chem. **16**, 290 (1936).
(265) ZACHAREWICZ, W.: Roczniki Chem. **17**, 630 (1937).