205. *Selenium Dioxide, a New Oxidising Agent. Part V. Some Further Oxidations.*

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The original discovery of the formation of 1 : 2-diketones by the action of selenium dioxide on ketones has been extended, in this series of papers (J., 1932, 1875, 2342; 1933, 391; 1934, 844) and by several other workers, to include many different types of reaction. Selenium dioxide is a relatively vigorous oxidising agent, particularly at high temperatures, and it is therefore surprising that unstable, highly reactive compounds, *e.g.*, mesoxalic ester and ketohydroxysuccinic ester, can be prepared by its use. Intermediate compound formation possibly plays an important part in this specific reactivity, for in many of the oxidations unstable organoselenium compounds are formed. Support for this view is provided by the reaction of acetophenone with selenium oxychloride (Nelson and Jones, *J. Amer. Chem. Soc.*, 1930, **52**, 1588), in which diphenacylselenium dichloride, $(C_6H_5{\cdot}CO{\cdot}CH_2)_2SeCl_2$, is formed, and by the fact that selenium oxychloride will also react with acetone to give methylglyoxal. To explain the varied reactivity of selenium dioxide on this theory, however, it would be necessary to postulate the existence of many different types of unstable intermediate compounds. Further, if intermediate compound formation is the necessary first step in the reaction, then the second must involve, in many cases, a very complicated addition of oxygen. This suggests that intermediate compound formation is not an essential part of the process, but rather that we must look for an explanation of this reactivity of the dioxide in some property of the selenium atom itself. It has been shown (Emeléus and Riley, *Proc. Roy. Soc.*, 1933, *A*, **140**, 378) that ammonia, carbon disulphide, hydrogen sulphide, and a large number of organic compounds all burn with similar flames when heated in selenium dioxide vapour. These flames all give similar spectra, which are characteristic of selenium and perhaps also of its oxide, but not of the substance undergoing oxidation. This remarkable phenomenon suggests that selenium dioxide possesses the property of providing the compounds undergoing combustion with oxygen atoms in a very low energy state. If the dioxide retains this property at lower temperatures, *i.e.*, at the temperatures at which it possesses its specific oxidising reactivity, then it is easily understood why certain unstable compounds can be formed.

The dehydrogenating action of selenium dioxide on ethyl succinate (J., 1933, 391) and acetonylacetone (Armstrong and Robinson, J., 1934, 1650) and particularly its reaction with dibenzyl and stilbene described in the present paper, indicate that the first process in many of the oxidations must be the removal of activated hydrogen atoms. This stage may or may not be followed by the addition of oxygen in a low energy state, according to the nature of the dehydrogenated product. All the reactions reported are, of course, readily formulated on this view; *e.g.*, Fisher (*J. Amer. Chem. Soc.*, 1934, **56**, 2056) has reported the formation of triphenylcarbinol from triphenylmethane. This can be represented quite simply as follows (the activated molecules being marked by an asterisk), $\mathrm{Ph_3CH} + \mathrm{SeO_2}^* \longrightarrow \mathrm{Ph_3C}{-} + \overset{\curvearrowleft}{\mathrm{HO}{-}} + \mathrm{SeO}^* \longrightarrow \mathrm{Ph_3C{\cdot}OH}$, or the reaction might be initiated by a collision between a selenium dioxide molecule and an activated triphenylmethane molecule. This mechanism suggests the possibility of the reaction being accompanied by chemiluminescence. This has been observed at low temperatures in only one case, namely, the oxidation of ammonia (Emeléus and Riley, *loc. cit.*).

The present paper describes further examples of the oxidising reactions of selenium dioxide.*

Experimental.

Ethyl Acetonedicarboxylate.—This ester (27 g.) and selenium dioxide (11·9 g.; 1·25 mols. : 1) were refluxed on a steam-bath for 24 hours and then for $1\frac{1}{2}$ hours in an oil-bath at 110°. The

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* A summary of papers published to date on the oxidising properties of selenium dioxide is included in *The Scientific Journal of the Royal College of Science*, 1935 (Arnold & Co.).

deep red liquid was decanted from the precipitated selenium and distilled, first at atmospheric pressure, 4 c.c. of alcohol and water being collected, and then in a vacuum. A fraction (6 c.c.), b. p. 70°/24 mm.—145°/30 mm., was collected; excessive decomposition then occurred. Redistilled, this fraction gave 2 c.c. of a bright yellow liquid, b. p. 90°/33 mm., having an evil, garlic-like smell, followed by a pale brown fraction, b. p. 90—200°/33 mm., which could not be redistilled without decomposition. The latter contained evil-smelling organoselenium compounds and, on standing in the air for some days, deposited crystals of oxalic acid hydrate. The bright yellow fraction gave with aqueous phenylhydrazine acetate the 4-phenylhydrazone of 4 : 5-diketo-1-phenyl-3-methyl-4 : 5-dihydropyrazole (Found : C, 69·0; H, 5·2. Calc. : C, 69·0; H, 5·0%), which on twice recrystallising from alcohol gave orange-red needles, m. p. 155°. This fraction was therefore ethyl αβ-diketobutyrate, the osazone of which is known to give the above pyrazole (see Knorr and Reuter, *Ber.*, 1894, **27**, 1176; Wahl, *Compt. rend.*, 1904, **138**, 1222). Presumably the selenium dioxide oxidised the acetonedicarboxylic ester in the normal manner to the αβ-diketoglutarate, which underwent hydrolysis and decarboxylation to form ethyl αβ-diketobutyrate.

Ethyl Malate.—The oxidation of this ester was studied in order to compare its behaviour with that of ethyl succinate (J., 1933, 391) and ethyl tartrate (J., 1934, 844). Ethyl *dl*-malate (20 g.) and selenium dioxide (3·90 g.; 3 mols. : 1) were refluxed at 120—130° for 5 hours, 2·0 g. of selenium (72%) being precipitated. The resulting liquid was decanted, the residual selenium washed with ether, and after removal of the ether, the combined liquids were distilled in a vacuum. Water and alcohol distilled first, followed by a bright yellow liquid. Two fractions were collected : (A), b. p. 120—164°/17 mm. (10 c.c.), and (B), b. p. 165—195°/17—24 mm. (2 c.c.). At higher temperatures decomposition occurred, leaving a tarry seleniferous residue. On refractionating A and B a liquid (C), b. p. 132—139°/24 mm., was obtained which gave with aqueous phenylhydrazine the 4-phenylhydrazone of ethyl 4 : 5-diketo-1-phenyldihydropyrazole-3-carboxylate, which on twice recrystallising from alcohol had m. p. and mixed m. p. 153·5° (Found : C, 64·4; H, 4·8. Calc. : C, 64·3; H, 4·8%). This compound might have been produced by the action of phenylhydrazine on either ethyl diketosuccinate or ethyl ketohydroxysuccinate. The latter on hydrolysis has been shown (J., 1934, 844) to give tartaric acid. The above liquid after hydrolysis for 2 hours with dilute hydrochloric acid gave a negative result with Fenton's test, indicating that (C) contained ethyl diketosuccinate. Support was obtained for this view by the addition to (C) of alcoholic hydroxylamine hydrochloride and a nickel salt. On the addition of alkali a small quantity of a nickel dioxime was obtained. On saponifying a further quantity of (C) with methyl-alcoholic potash, some fumaric acid, m. p. and mixed m. p. 287—289° (in a sealed tube), was obtained (Found : C, 41·2; H, 3·5. Calc. : C, 41·4; H, 3·4%). This shows that selenium dioxide also dehydrates ethyl malate. Oxalic acid was also found amongst the products of hydrolysis. This might have been formed by the hydrolysis of ethyl oxaloacetate, a possible oxidation product. No such product could, however, be detected.

Further oxidations were carried out with ethyl malate and selenium dioxide in the ratios 1·5 mols. : 1 and 1 mol. : 1·5, the latter oxidation in the presence of dioxan. The following additional products were detected; malic acid, ethyl hydrogen malate (not previously reported; an extremely deliquescent solid, b. p. 240°/35 mm., which gave malic acid on saponification with caustic potash), and the monoethyl ester of mesoxalic acid, identified by means of its phenylhydrazone, which gave yellow needles on recrystallisation from alcohol, m. p. 114° (Found : C, 55·5; H, 5·2. Calc. : C, 55·9; H, 5·1%).

The products of the oxidation of ethyl malate thus vary with the proportions of the reactants employed. With excess of ester, ethyl diketosuccinate was produced together with some ethyl fumarate. With the dioxide in excess, oxalic acid and ethyl hydrogen mesoxalate were also found. A large amount of decomposition and the formation of complex organoselenium compounds also occurred.

Ethyl β-Phenylpropionate.—It has already been shown (J., 1933, 391) that ethyl succinate on oxidation with selenium dioxide yields principally ethyl fumarate and not a ketonic compound. A similar observation was made by Armstrong and Robinson (*loc. cit.*), who reported the formation of diacetylethylene from acetonylacetone. This and the following section provide still further examples of this type of reaction.

Ethyl β-phenylpropionate (25·2 g.) and selenium dioxide (5·3 g.; 3 mols. : 1) were refluxed together at 200° for 5 hours. A considerable amount of carbon dioxide was evolved, and the theoretical amount of selenium precipitated. The resulting orange-coloured liquid was twice fractionated in a vacuum, 13 c.c. (boiling up to 143°/23 mm.) of unchanged ethyl β-phenylpropionate, 4 c.c., b. p. 143—160°/21 mm. (A), and 2 c.c., b. p. 160—175°/21 mm. (B), being obtained. The last few drops of the distillate solidified in the condenser to white crystals of a mixture of β-phenylpropionic and cinnamic acids. A sharp separation of the liquid products by distillation was not possible. Ethyl β-phenylpropionate has b. p. 127°/15 mm., and ethyl cinnamate, 144°/15 mm. Both fractions (A) and (B) slowly decolorised a solution of bromine in carbon tetrachloride. In order to detect the presence of ethyl cinnamate, (B) was hydrolysed with methyl-alcoholic caustic potash, followed by hydrochloric acid. When the resulting crude acid was fractionally crystallised thrice from light petroleum, 0·5 g. of cinnamic acid (m. p. 133°. Found : C, 73·1; H, 5·5. Calc. : C, 73·0; H, 5·4%) was obtained. On evaporation of the mother-liquors, 1·3 g. of β-phenylpropionic acid, m. p. and mixed m. p. 50°, were obtained. Fraction (A) gave in a similar way 0·5 g. of cinnamic acid and 2·3 g. of β-phenylpropionic acid. The total yield of cinnamic acid was 8% of the theoretical amount, calculated on the selenium dioxide used, showing that dehydrogenation had occurred to an appreciable extent.

Dibenzyl.—This compound (30 g.) and selenium dioxide (30 g.) were refluxed at 200° for 9 hours. The resulting liquid was distilled, first at atmospheric pressure, 4 g. of a mixture of benzene, benzaldehyde, water, and a little dibenzyl being obtained, and then under reduced pressure, two fractions being collected, (A), b. p. 185—200°/25 mm., and (B), b. p. 200—215°/25 mm. Fraction (B), on recrystallising from light petroleum (b. p. 40—60°), gave 2·5 g. of benzil, m. p. 94°. Its bisphenylhydrazone had m. p. 232° (Found : C, 79·7; H, 5·7. Calc. : C, 80·0; H, 5·6%). Fraction (A) was fractionally crystallised from glacial acetic acid, 4·2 g. of stilbene, m. p. 124° (Found : C, 92·9; H, 6·8. Calc. : C, 93·3; H, 6·7%), being obtained. It gave an antimony trichloride derivative, m. p. 105—106°. The mother-liquors from this fractionation were diluted with a large excess of cold water, and the yellow precipitate recrystallised from light petroleum (b. p. 40—60°) and then from alcohol. In this way, a further 7·5 g. of benzil, were obtained and a further 2 g. of dibenzyl recovered.

The oxidation was repeated, 9 g. of selenium dioxide and 30 g. of dibenzyl being refluxed for 6 hours. The product was treated in a similar manner, 2·8 g. of benzil and 5·1 g. of stilbene being obtained, *i.e.*, yields of 33% and 17·5% respectively calculated on the dioxide used.

The formation of both ketonic and unsaturated products in this reaction is interesting. The following results indicated that in the oxidation of dibenzyl, dehydrogenation to stilbene is the first step, followed by the oxidation of stilbene to benzil.

Stilbene (3 g.) and selenium dioxide (3 g.) were heated together at 190—200° for 7 hours. The resulting liquid was decanted, and the precipitated selenium washed with ether. The liquid and washings were evaporated to remove ether and the residue was dissolved in cold acetic acid. Excess of aqueous phenylhydrazine acetate was added and, after heating on the water-bath and cooling, the precipitated benzil bisphenylhydrazone, m. p. 220°, was filtered off, dried, and weighed. 5·5 G. of this derivative, *i.e.*, 86·6% of the theoretical yield, were obtained. A similar experiment with 6·4 g. of dibenzyl and 10 g. of selenium dioxide indicated a 73·3% yield of benzil.

Ethyl Mandelate.—The ester (25 g.) and selenium dioxide (6 g.) were refluxed together at 150° for 2½ hours. The liquid product was decanted and fractionated in a vacuum, most of it distilling at 155—165°/20 mm. Excess of sodium bisulphite solution was added to the distillate and the precipitated bisulphite compound was washed with a little ether and water and then decomposed with 20% sulphuric acid in the presence of benzene. The resulting liquid product was fractionated in a vacuum, 11·5 g. (60% theoretical) of ethyl benzoylformate, b. p. (at atm. pressure) 255—256°, being obtained. This gave an oxime, m. p. 112° on recrystallisation from water (Found : N 7·4. Calc. : N, 7·2%).

Ethyl Phenylacetate.—The ester (30 g.) and selenium dioxide (14 g.) were treated in a manner similar to the above. The dioxide was not reduced quite so readily and 5—6 hours were necessary for its complete reduction. 7·6 G. (34% theoretical) of ethyl benzoylformate were obtained. Thus, ethyl mandelate passed more readily into ethyl benzoylformate, on oxidation with selenium dioxide, than did ethyl phenylacetate.

Anthracene.—The hydrocarbon (20 g.) and selenium dioxide (19 g.) were mixed with nitrobenzene (65 c.c.) and heated at 160° for 3 hours. Nitrobenzene was then removed by steam distillation and the black tarry residue was extracted thrice with hot glacial acetic acid. When the hot extract was evaporated somewhat and allowed to cool, crude anthraquinone crystallised. On purification by recrystallisation and sublimation, it gave m. p. and mixed m. p. 284° (Found : C, 80·8; H, 3·8. Calc. : C, 80·8 ; H, 3·8%). Yield, 17 g. (73% of the theoretical). The theoretical amount of selenium remained after the acetic acid extraction. In dioxan, ethylene glycol, and ethyl alcohol the oxidation did not proceed at an appreciable rate. Phenanthrene was not so readily oxidised nor could phenanthraquinone be identified in the oxidation product.

The Reaction of Selenium Dioxide with Aromatic Amines.—At temperatures below their boiling points many aromatic amines reacted vigorously with selenium dioxide. When aniline was added to an alcoholic solution of selenium dioxide, and the excess of alcohol removed in a vacuum, a cream-coloured crystalline solid was obtained. When heated gently, this substance decomposed, without the liberation of aniline, forming a dark purple resin, sparingly soluble in alcohol and in water, but insoluble in other common solvents; it could not be recrystallised. In order to exclude the formation of aniline selenite, the above experiment was repeated with thoroughly dried reagents, methyl alcohol being substituted for ethyl, as it was more readily obtained in the anhydrous condition. Selenium dioxide was dissolved in a little dry methyl alcohol, and a weighed quantity of dry aniline added, the amount being varied in different experiments. Some of the alcohol was evaporated in a vacuum; a white crystalline compound was then deposited. When equimolecular quantities of selenium dioxide and aniline were employed, and the product was dried on a porous plate (it was too unstable to be washed with alcohol or ether), it was obtained in cream-coloured needles, m. p. 56°. Decomposition occurred a few degrees above the melting point (Found : C, 35·4; H, 4·8; N, 5·9; Se, 33·1. $C_7H_{11}O_3NSe$ requires C, 35·5; H, 4·7; N, 5·9; Se, 33·5%). After a few days, the *substance* turned grey and a faint smell of nitrobenzene developed. When heated, the substance decomposed, giving a purple resin, slightly soluble in chloroform, forming a deep purple solution. With *p*-toluidine instead of aniline, a similar compound, m. p. 67°, was obtained, too unstable for purification.

When methylaniline was added to a solution of selenium dioxide in methyl alcohol, a considerable amount of heat was evolved, but no solid compound could be obtained on removal of the excess of methyl alcohol in a vacuum. On standing, the solution became dark purple.

The composition of the compound obtained from aniline indicated that it was formed by the combination of one molecule each of aniline, selenium dioxide, and methyl alcohol. This suggested that selenium dioxide dissolved in methyl alcohol with the intermediate formation of methyl hydrogen selenite. This was confirmed by dissolving selenium dioxide in methyl alcohol and evaporating the solution in a vacuum at room temperature. White crystalline *methyl hydrogen selenite* (or *methylselenonic acid*), m. p. 42°, was obtained (Found : Se, 55·2. $CH_3{\cdot}HSeO_3$ requires Se, 55·4%). A similar compound was obtained by Hinsberg (*Annalen*, 1890, **260**, 40) when a solution of selenium dioxide in ethyl alcohol was evaporated over calcium chloride. Its composition corresponded roughly to $C_2H_6O_3Se$, and on standing over concentrated sulphuric acid the crystals crumbled, leaving selenium dioxide. Hinsberg did not decide whether the substance was a definite compound or selenium dioxide containing alcohol of crystallisation, since he could not prepare any salt in the pure condition.

No methyl alcohol could be obtained from the above aniline compound when it was carefully distilled with aqueous sodium hydroxide solution. This indicated that it was not an aniline salt of methyl hydrogen selenite, but perhaps the aniline salt of methylselenonic acid. The unstable nature of the compound prevented the confirmation of this view.

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