105. *Selenium Dioxide, a New Oxidising Agent. Part III. Its Reaction with Some Alcohols and Esters.*

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Although selenium dioxide is not reduced by the simpler aliphatic alcohols at their boiling points, reaction occurs at slightly higher temperatures and the possibility of the direct formation of glyoxals (see Part I; J., 1932, 1875) from the corresponding alcohols led to the investigation of the oxidation products from ethyl, *n*-propyl, and *n*-butyl alcohols. The yield of a particular oxidation product was largely determined by its stability in the presence of excess selenium dioxide at the temperature of the reaction. Whereas ethyl alcohol gave an appreciable quantity of glyoxal when oxidised at 200°, only traces of methyl- and ethyl-glyoxal were formed under similar conditions from propyl and butyl alcohol respectively. The reactions with alcohols were much more complex and sensitive to temperature changes than those with aldehydes and ketones (Part I), the formation of dialkyl selenites, solids of the formula $(CH_2)_n$, glyoxals, and oxides of carbon occurring.

The reaction with benzyl alcohol proceeded, but not completely, at the b. p. of the alcohol and gave benzaldehyde in which no trace of benzoic acid could be detected.

Ethyl malonate behaved similarly to the aldehydes and ketones. The relative instability of the mesoxalic ester formed necessitated the precise definition of the experimental conditions. The method proved, however, a much easier and simpler way of obtaining the keto-ester than those previously described.

Ethyl succinate behaved abnormally. Although indications of the formation of a trace of ethyl diketosuccinate were obtained, the principal oxidation product was a mixture of ethyl fumarate and ethyl hydrogen fumarate in 40% yield. The reason for this was probably that both methylene groups in the succinic ester were equally activated by the proximity of the negative carbethoxy-groups and consequently were attacked more or less simultaneously. The removal of a hydrogen atom from each resulted in the formation of the double bond before further oxidation could occur. The resulting fumaric esters were not oxidised further at the temperature of the reaction (170°). Again it was necessary precisely to define the conditions of experiment. (Cf. Fischer, *Ber.*, 1927, **60**, 2260, for another direct conversion of succinic into fumaric acid by biological means.)

EXPERIMENTAL.

Ethyl Alcohol.—EtOH vapour was passed over SeO_2 heated to a max. temp. of 230° in a glass tube (see Part I, *loc. cit.*; Part II, *ibid.*, p. 2342). The alcohol vapour very readily inflamed in the SeO_2 vapour (see Emeléus and Riley, *Proc. Roy. Soc.*, in the press). The max. yield of glyoxal was 5%, calc. on the SeO_2 reduced. CO and CO_2 were also formed. The yield of glyoxal fell considerably when inflammation occurred, indicating that this was accompanied by more complete oxidation.

SeO_2 (112 g.) and abs. EtOH (240 c.c.) were heated in a 2 l. autoclave for 2½ hr. to a max. temp. of 150°, a max. press. of 11 kg./sq. cm. resulting. A permanent press. of 1·4 kg./sq. cm. remained on cooling (CO and CO_2). Only partial reduction had occurred, 12 g. Se having been pptd. The residual liquid was filtered, dried with Na_2SO_4, and fractionated. After the excess of EtOH had been removed, a fraction, b. p. 175°, was obtained. On refractionation it gave 20 c.c., b. p. 100°/50 mm., of ethyl selenite contaminated with a little EtOH, which could not be removed completely owing to the instability of the compound (Michaelis and Landmann, *Annalen*, 1887, **241**, 150).

The expt. was repeated with 50 g. SeO_2 and 750 c.c. EtOH, heated to a max. temp. of 200° for 2½ hr. The max. press. was 30 kg./sq. cm. The reduction of the SeO_2 was complete. On removal of the excess of EtOH, a syrupy liquid remained which contained glyoxal in 41% yield (calc. on SeO_2 reduced), determined as described in Part I (*loc. cit.*).

A similar expt. employing 50 g. SeO_2, 500 c.c. EtOH, a max. temp. of 205°, and 4 hrs.' heating gave only 24% glyoxal. Mixed with the pptd. Se and suspended in the resulting liquid was a small amount of a sand-coloured solid, m. p. 52° after recrystn. from abs. EtOH [Found: C, 84·6; H, 14·1. $(CH_2)_n$ requires C, 85·7; H, 14·3%].

When SeO_2 reacted with an equational quantity of EtOH at 200°, a small quantity of ethyl ether was formed.

Although SeO_2 was not reduced by boiling EtOH, if a sufficient excess of the dioxide was employed the temp. rose to over 140° before all the liquid had distilled. At these higher temp. considerable reduction of the dioxide occurred, accompanied by the formation of appreciable quantities of glyoxal.

n-*Propyl Alcohol.*—*n*-PrOH (550 c.c.) and SeO_2 (140 g.) were heated in an autoclave for 4½ hr. at 155°. The resulting liquid was diluted with Et_2O, filtered from 19 g. of pptd. Se, dried with Na_2SO_4, and fractionated. 320 C.c. of PrOH were recovered, and 40 c.c. of *propyl selenite*, b. p. 132—133°/25 mm., obtained [Found : C, 33·9; H, 6·4; Se, 35·8; *M*, 198 in AcOH and 411 in C_6H_6. $(C_3H_7)_2SeO_3$ requires C, 33·8; H, 6·7; Se, 37·1%; *M*, 213. The low Se figure was due to a small amount of decomp. which occurred during distillation]. Its general chemistry was in agreement with its formulation as propyl selenite. The liquid had a pleasant odour and was stable at room temp. when dry.

A similar expt. was carried out with SeO_2 (125 g.) and *n*-PrOH (500 c.c.) at 210° for 5 hr. A max. press. of 32 kg./sq. cm. was registered. After cooling, the press. was 4·2 kg./sq. cm. (CO and CO_2). 84 G. of Se had been pptd. Mixed with the Se and suspended in the liquid were about 2 g. of a sand-coloured solid, similar to that obtained with EtOH, m. p. 60° after four crystns. from PrOH [Found : C, 85·9; H, 14·2. $(CH_2)_n$ requires C, 85·7; H, 14·3%. *M* (Rast) gave $n = ca.$ 30]. The liquid oxidation product, dried over CaO and fractionated, gave a few drops, b. p. about 57°, having an aldehydic odour. The excess of PrOH was collected at 97°. The residue was taken up in Et_2O and fractionated in vac.; 6 c.c., b. p. 100—130°/20—30 mm., and 3 c.c., b. p. 130—160°/20—30 mm., and a small amount which solidified in the condenser were obtained. The liquids were pale yellow and viscous, contained no Se, and were probably complex polymerised products. No methylglyoxal could be detected.

SeO_2 was refluxed with PrOH for several hr. Only a trace of Se was pptd. The excess of PrOH was distilled off up to 120°; oxidation then occurred and a small amount of methylglyoxal was detected, by means of its phenylhydrazone, in the distillate above this temp.

n-Butyl Alcohol.—Similar expts. with *n*-butyl alcohol indicated the formation of butyl selenite, which was not sufficiently stable to permit of its purification, a trace of ethylglyoxal, and a small amount of a sand-coloured hydrocarbon, similar to that obtained from EtOH and PrOH.

Benzyl Alcohol.—SeO_2 (56 g.) and $CH_2Ph{\cdot}OH$ (108 c.c.) were refluxed for 10 hr. Less than half (16·5 g.) of the Se present was pptd. The resulting liquid was treated with H_2O, and the whole extracted with Et_2O. The extract was dried with Na_2SO_4, the ether removed, and sat. $NaHSO_3$ aq. added (yield of bisulphite compound, 81 g. Theo. wt. of benzaldehyde bisulphite compound calc. on pptd. Se, 87 g.). Estimation of the benzaldehyde by means of *p*-nitrophenylhydrazine showed 100% conversion (on Se pptd.).

Ethyl Malonate. Preparation of Ethyl Mesoxalate.—Preliminary expts. showed that when SeO_2 and malonic ester were refluxed together, an exothermic reaction occurred with the formation of mesoxalic ester in 10—12% yield and of CO and CO_2 in considerable quantity. The following reactions probably accounted for the poor yields :

$$CH_2(CO_2Et)_2 + H_2O = CH_3{\cdot}CO_2Et + EtOH + CO_2 \text{ at } 150^\circ$$

(Hjelt, *Ber.*, 1880, **13**, 1949). A small amount of EtOAc was always detected in the distillate from the reaction carried out at the b. p. of the malonic ester (195°).

$$CO(CO_2Et)_2 = (CO_2Et)_2 + CO \text{ at } 180^\circ$$

(Anschütz and Pauly, *Ber.*, 1894, **27**, 1304). It was therefore advisable to carry out the oxidation at the lowest practicable temp.

Isolation of the mesoxalic ester, as the hydrate, by extraction with H_2O, although a convenient method, introduced a difficulty owing to the ready hydrolysis of the ester, which was accelerated by the presence of a trace of SeO_2 in the extract. The following method was therefore adopted. Ethyl malonate (40 g.; 2 mols.) and SeO_2 (14 g.; 1 mol.) were heated together at 120—130° for 2 hr. : 7·2 g. of Se were pptd. and some CO_2 was evolved. The liquid was decanted and distilled in vac., giving the fractions : (A) up to 80°/45 mm., 2 c.c.; (B) 80—130°/36 mm., 25 c.c.; and (C) 130—230°/36 mm., 4 c.c. Fraction C was a complex, garlic-smelling mixture of Se-containing compounds. Fraction B was extracted with H_2O (7×10 c.c.) and the extracts were quickly evaporated separately until they became viscous and yellow. On cooling in ice, they crystallised slowly, giving white ethyl mesoxalate hydrate, m. p. 56° (Found : C, 43·6; H, 6·2. Calc. : C, 43·7; H, 6·3%). Yield, 7·75 g. (32·3% of the theo. amount calc. on SeO_2 used). This method of extraction and evaporation localised the effect of any trace of SeO_2 to the first aq. extract. On drying the liquid remaining from the aq. extraction, 12 c.c. of ethyl malonate, b. p. 193—198°, were recovered.

Ethyl Succinate. Preparation of Ethyl Hydrogen Fumarate and Fumaric Acid.—SeO_2 (112 g.) and ethyl succinate (87 g.) (N.B. The SeO_2 was here in excess, 2 mols. : 1. In all the oxidations hitherto described, the SeO_2 has been less than the equational quantity. In the present case fumaric ester was produced, even when excess of ethyl succinate was used, but the above ratio gave the max. yield.) were heated together at 170° for 10 hr. After cooling, the product was extracted several times with Et_2O, the Et_2O removed, and the residual liquid distilled in vac., giving 3 c.c. of Et_2O, EtOH, H_2O, and a little ester, b. p. up to 85°/30 mm., and 35 g., b. p. up to 150°/30 mm. (fraction A). At this temp. the distillate began to solidify, and 17·4 g. of ethyl hydrogen fumarate, m. p. 60—63°, containing traces of Se and succinic acid, were collected : it had m. p. 66° after two recrystns. from petroleum (b. p. 80—100°) (Found : C, 49·9; H, 5·5; equiv. from Ag salt, 138; *M*, Rast 162. Calc. : C, 50·0; H, 5·6%; equiv., 144), and gave fumaric acid, m. p. 286—289° (in a sealed tube), on hydrolysis.

Fraction A, which had a decided acid reaction, was refractionated, mostly at 110—112°/22 mm.; at 138°/22 mm. 3·05 g. of ethyl hydrogen fumarate were collected. The liquid fraction was again distilled, giving 25·6 g., b. p. 108°/18 mm., 5 g., b. p. 108—118°/18 mm., and a residue (0·4 g.), which solidified (total yield of monoester, 20·9 g.; 29% of theo. amount calc. on the succinic ester used).

As ethyl succinate and ethyl fumarate have the same b. p., in order to determine the amount of the latter in the liquid fractions, these were hydrolysed and the acid product fractionally crystallised from H_2O : after three crystns., fumaric acid, m. p. and mixed m. p. 289°, was obtained in 11·4% yield.

CO_2 was evolved during the initial oxidation, and some succinic acid was obtained in the final separation of the fumaric acid. Under the conditions of the above oxidation, all the SeO_2 was not reduced, unattacked crystals being visible at the end of the reaction. It is possible that the excess of dioxide served to absorb the H_2O produced in the reaction. H_2SeO_3 is readily sol. in ethyl succinate (it can be recrystallised from this solvent) and is only slightly reduced at the b. p. of the solution, whereas SeO_2 under similar conditions is readily attacked.

To disprove the possibility that the fumaric ester was produced by the dehydrogenating action of the Se and not by the oxidising action of the dioxide, ethyl succinate was boiled with Se for 3 days : no trace of fumaric ester was found, nor was H_2Se evolved.

The Allotropy of Selenium.—The Se pptd. from the dioxide by low-boiling org. liquids such as acetone and CH_3·CHO was in the vitreous form. That obtained from EtOH under press. at 200° was in fine, grey, shining crystals of the " metallic " variety, some 1 mm. in length. The Se was also pptd. in the grey " metallic " form by reduction of the dioxide with succinic ester. Boiling succinic ester, in the course of some hrs., transformed vitreous Se, which was almost liquid at the temp., into the grey cryst. variety. The crystals formed in large clusters some distance from the surface of the vitreous Se. A grey amorphous variety of Se has been formed in certain expts. with boiling AcOH and Ac_2O. It melted at 220°, so was probably a finely divided variety of the grey cryst. form (cf. Saunders, *J. Physical Chem.*, 1900, **4**, 424; and the papers of de Coninck and co-workers, 1905—1906). It is probable that many specimens of Se prepared by reducing oxy-compounds with org. compounds are appreciably contaminated with org. matter, as the following note shows.

Note on the Recovery of Selenium Dioxide.—Se which had been pptd. during the oxidation of a large variety of org. compounds always reacted more vigorously than ordinary Se when treated with HNO_3 in the initial step of the recovery of SeO_2. Recently a specimen of vitreous Se, formed in the oxidation of CH_3·CHO to glyoxal, was heated rather quickly in O with the view of burning it to dioxide. A vigorous explosion occurred. The vitreous Se was quite dry and looked pure, but the cause of the explosion was, no doubt, the rapid oxidation of a trace of org. matter in the Se, the reaction being catalysed by the Se, a reaction not dissimilar to that occurring when ordinary black gun-powder explodes. It is therefore advisable to heat the Se slowly, almost to its b. p. in air, until all the org. matter is expelled, before any attempt to burn it is made. The HNO_3 method is, however, the more convenient in the laboratory.

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