470. The Action of Selenious Acid on Alkyl Ethers of Phenols.

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In the presence of water selenium dioxide reacts with aryl alkyl ethers to yield the corresponding di-*p*-alkoxyphenyl selenides.

The use of anisole as a solvent for a reaction in which selenium dioxide was being employed as an oxidising agent led us to suspect that interaction between these two compounds was taking place. Accordingly the matter was investigated and the results are now presented.

When anisole is heated at temperatures somewhat below its boiling point with ordinary—*i.e.* not recently resublimed—selenium dioxide a reaction occurs resulting in the separation of water and the development of a red colour. From the reaction mixture di-*p*-methoxyphenyl selenide can be readily isolated.

In marked contrast, when anisole is heated with freshly sublimed selenium dioxide no reaction occurs, even during 20 hours at 130—150° and the selenium dioxide remains largely undissolved. When, however, a few drops of water are added and the mixture reheated reaction soon sets in. Since water is necessary to initiate the reaction it seems likely that the ether is attacked by selenious acid rather than by selenium dioxide. Subsequent experiments indicated that the maximum yield of di-*p*-methoxyphenyl selenide (about 20%) is obtained when the added water amounts to one molecular proportion.

It seems reasonable to suppose that di-*p*-methoxyphenyl selenoxide or di-*p*-methoxyphenylselenium dihydroxide is formed intermedially during the conversion of anisole into di-*p*-methoxyphenyl selenide and to obtain evidence bearing on this view two experiments were performed.

The first one showed that when di-*p*-methoxyphenylselenium dihydroxide in anisole solution was heated at 130—150° for 15 hours only some 10% had been converted into di-*p*-methoxyphenyl selenide. It has to be remembered, however, that the reaction between anisole and selenious acid is a complex one during which selenium is, in all probability, liberated and this suggested the second experiment. This showed that di-*p*-methoxyphenylselenium dihydroxide, dissolved in 50% acetic acid containing in suspension freshly precipitated selenium, heated for 3 hours was converted almost completely into di-*p*-methoxyphenyl selenide—no di-*p*-methoxyphenylselenium dihydroxide was recovered.

In this reaction and in the reactions between selenious acid and other phenolic ethers the selenides formed are always accompanied by red oily by-products of an intractable nature.

By action of selenious acid the following ethers have been converted into the corresponding selenides: phenetole, *o*- and *m*-dimethoxybenzene, 1- and 2-methoxynaphthalenes, and *p*-bromoanisole; *o*-dimethoxybenzene yielded a mixture of the selenide and the diselenide whilst *p*-dimethoxybenzene and diphenyl ether yielded selenium-containing products of high melting points which, owing to difficulties of purification, were not further examined.

Dimethoxyphenyl selenide has been previously prepared by reduction of the dichloride resulting from the action of selenium oxydichloride on anisole (Alquist and Nelson, *J. Amer. Chem. Soc.*, **1931**, **53**, 4033) but the position of the selenium atom was left undetermined. That it occupies the *pp'*-position has now been established since diazotised *p*-anisidine is converted by the action of potassium polyselenide into di-*p*-methoxyphenyl selenide identical with that obtained from anisole and selenious acid. It seems probable, therefore, that the selenides obtained by the action of selenious acid on *o*- and *m*-dimethoxybenzenes are bis-3 : 4- and bis-2 : 4-dimethoxyphenyl selenide respectively.

In order to characterise the various selenides the following derivatives were prepared: di-*p*-methoxyphenylselenium dibromide; and di-*p*-methoxyphenylselenium dihydroxide, (*a*) by the action of sodium hydroxide on the dibromide, (*b*) by the action of hydrogen peroxide on the selenide.

The corresponding derivatives of di-*p*-ethoxyphenyl selenide were prepared by the same methods.

The selenide obtained from *o*-dimethoxybenzene does not combine with bromine to yield a stable dibromide but is converted by hydrogen peroxide into the dihydroxide.

EXPERIMENTAL.

The various ethers were purified by shaking them with sodium hydroxide followed by distillation, or recrystallisation; the selenium dioxide was purified by sublimation.

Non-interaction of Anhydrous Selenium Dioxide and Anisole.—A mixture of freshly sublimed selenium dioxide (50 g.) and anisole (125 g.) was stirred and maintained at 130—150° for 20 hours but no reaction occurred. A similar negative result was obtained when dioxan was used as a diluent.

Action of Selenium Dioxide on Anisole in the Presence of Water.—A mixture of selenium dioxide (50 g.), water (8·2 g., 1 mol.), and anisole (125 g., 2·5 mols.) was maintained at 130—150° for 20 hours and the unchanged anisole removed in a current of steam. The semi-solid non-volatile residue was dissolved in ether (Norit), the solution dried, and the solvent removed. The orange solid residue (27 g.; 20%, on selenium dioxide used), after several crystallisations from alcohol, yielded di-*p*-methoxyphenyl selenide as colourless, glistening leaflets (14 g.), m. p. 56·5—58° (Found: C, 57·1; H, 5·0; OMe, 21·0. Calc. for $C_{14}H_{14}O_2Se$: C, 57·3; H, 4·8; OMe, 21·2%).

Di-*p*-methoxyphenyl selenide was obtained by the action of potassium polyselenide on diazotised *p*-anisidine following the procedure given in *Org. Synth.*, 1938, **18**, 28, for the preparation of diphenyl selenide. It was obtained in 10% yield and had m. p. 56—57° alone or when mixed with the selenide prepared from anisole.

In a similar manner diazotised *o*-anisidine and potassium polyselenide yielded *di*-o-*methoxyphenyl diselenide* in 18% yield. It separated from alcohol in pale yellow needles, m. p. 83—84° (Found: C, 44·9; H, 3·7. $C_{14}H_{14}O_2Se_2$ requires C, 45·2; H, 3·8%).

Di-p-*methoxyphenylselenium dibromide.* This compound is highly susceptible to moisture and consequently difficult to recrystallise. It is therefore best prepared in dilute solution from which it will separate in a pure crystalline condition. A solution of bromine (3 g.) in carbon disulphide (30 ml.) was added quickly to a solution of the selenide (1·0 g.) in the same solvent (30 ml.). Almost immediately di-*p*-methoxyphenylselenium dibromide separated in theoretical yield in orange-red prismatic rods, m. p. 118—120° (decomp.) (Found: C, 37·0; H, 3·0; Br, 36·6. Calc. for $C_{14}H_{14}O_2SeBr_2$: C, 37·1; H, 3·1; Br, 35·3%).

Di-p-*methoxyphenylselenium dihydroxide.* (*a*) When di-*p*-methoxyphenylselenium dibromide was triturated with sodium hydroxide solution it became pasty, lost colour, and soon set hard. The resulting dihydroxide separated from alcohol or benzene in colourless needles, m. p. 148° (Found: C, 51·6; H, 4·6. Calc. for $C_{14}H_{16}O_4Se$: C, 51·4; H, 4·9%). (*b*) Di-*p*-methoxyphenyl selenide (3 g.) was triturated with hydrogen peroxide (3 ml.; 30%) and a vigorous reaction set in with evolution of heat. The resulting dihydroxide, after crystallisation, had m. p. 148°, alone or mixed with the compound prepared as under (*a*). It was unchanged after being heated for 10 minutes at 220° (Alquist and Nelson, *loc. cit.*, give m. p. 54° for di-*p*-methoxyphenyl selenide, m. p. 125° for di-*p*-methoxyphenylselenium dibromide, and m. p. 134° for di-*p*-methoxyphenyl selenium dihydroxide).

The Action of Selenious Acid on Various Aryl Ethers.—*On phenetole.* A mixture of selenium dioxide (20 g.), water (3·2 ml.), and phenetole (55 ml.) after being heated at 120—140° for 20 hours and worked up as previously described yielded 20% of di-*p*-ethoxyphenyl selenide as needles, m. p. 61—62° (Alquist and Nelson, *loc. cit.*, give m. p. 60—62°) (Found: C, 60·3; H, 5·8; OEt, 26·2. Calc. for $C_{16}H_{18}O_2Se$: C, 60·1; H, 5·7; OEt, 28·1%).

Its dibromide formed bright red plates, m. p. 115° (decomp.), and its dihydroxide, prepared either by the action of sodium hydroxide on the dibromide or by the action of hydrogen peroxide on the selenide, formed plates, m. p. 172—173° (Alquist and Nelson, *loc. cit.*, give m. p. 148°) (Found: C, 54·4; H, 5·4. Calc.: C, 54·1; H, 5·7%).

On o-*dimethoxybenzene.* A mixture of selenium dioxide (10 g.), water (1·8 ml.), and *o*-dimethoxybenzene (25 g.) was heated at 130—150° for 20 hours and yielded a product which on fractional crystallisation from aqueous alcohol was separated into the more soluble *bis*-3 : 4-*dimethoxyphenyl selenide* (1·5 g.) and the less soluble *bis*-3 : 4-*dimethoxyphenyl diselenide* (12·9 g.).

The selenide, which separated as needles, m. p. 101—102·5° (Found: C, 54·1; H, 5·2. $C_{16}H_{18}O_4Se$ requires C, 54·4; H, 5·1%), reacted readily with hydrogen peroxide to give *bis*-3 : 4-*dimethoxyphenylselenium dihydroxide* which crystallised from alcohol in plates, m. p. 170—172° (Found: C, 49·7; H, 4·8. $C_{16}H_{20}O_6Se$ requires C, 49·6; H, 5·2%). The diselenide separated from alcohol in small prisms, m. p. 169—170° (Found: C, 44·9; H, 4·0. $C_{16}H_{18}O_4Se_2$ requires C, 44·5; H, 4·2%).

On m-*dimethoxybenzene.* This compound, treated as was the *o*-compound, gave *bis*-2 : 4-*dimethoxyphenyl selenide* (yield, 25%) as plates, m. p. 108—110°, from alcohol (Found: C, 54·6; H, 5·2. $C_{16}H_{18}O_4Se$ requires C, 54·4; H, 5·1%). Hydrogen peroxide had no action on this compound; bromine does not combine with it directly to give a coloured addition compound but effects a more complex reaction involving the evolution of hydrogen bromide.

On 1-*methoxynaphthalene and* 2-*methoxynaphthalene.* These gave, respectively, *di*-(1-*methoxynaphthyl*) *selenide* (28%) as pale yellow rods, m. p. 137—138°, from alcohol (Found: C, 67·4; H, 4·6. $C_{22}H_{18}O_2Se$ requires C, 67·2; H, 4·6%), and *di*-(2-*methoxynaphthyl*) *selenide* (17%) as colourless needles, m.p. 163°, from acetone–alcohol (Found: C, 66·9; H, 4·9%). Hydrogen peroxide had no effect on these selenides, and combination with bromine yielded oils.

On p-*bromoanisole.* This gave *di*-(5-*bromo*-2-*methoxyphenyl*) [or *di*-(2-*bromo*-5-*methoxyphenyl*)] *selenide* (22%) as colourless prisms, m. p. 150—151°, from alcohol (Found: C, 37·3; H, 2·9; Br, 35·0. $C_{14}H_{12}O_2Br_2Se$ requires C, 37·3; H, 2·7; Br, 35·4%).

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