

113. *Potassium Alkaneselenonates and Other Alkyl Derivatives of Selenium.*

By MARJORIE L. BIRD and FREDERICK CHALLENGER.

Methane-, ethane-, and propane-1-seleninic acids give the potassium salts of the corresponding alkaneselenonic acids, $R \cdot \text{SeO}_3\text{H}$, on oxidation with potassium permanganate. These eliminate selenious acid on treatment with hot dilute acid. Methaneselenonic acid is also formed on oxidation of dimethyl selenide with the same reagent. Alkaneseleninic acids, $R \cdot \text{SeO}_2\text{H}$, are formed on oxidation of dimethyl selenide with hydrogen peroxide or by the action of aqueous silver oxide on diethyl and di-*n*-propyl selenide dibromides. The dihydroxide or selenoxide, $(\text{CH}_3)_2\text{Se}(\text{OH})_2$ or $(\text{CH}_3)_2\text{SeO}$, is formed from dimethyl selenide by the action of concentrated hydrogen peroxide or of aqueous silver oxide on the dibromide. Dialkyl diselenides can be converted into methyl alkyl selenides by reduction with sodium and alcohol and treatment with methyl iodide. Dialkyl diselenides undergo fission with mercuric salts.

SOME of the alkylated derivatives of selenium described in this communication were prepared with a view to a study of their behaviour in bread cultures of certain moulds, particularly *Scopulariopsis brevicaulis* (see follow-

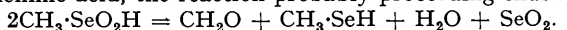
ing paper). Others were prepared in order to facilitate the identification of products of mould metabolism, or of the oxidation of the dialkyl selenides.

The method of Tschugaeff and Chlopin (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 364) for the preparation of alkyl selenides and tellurides (see Balfe, Chaplin, and Phillips, J., 1938, 341; Balfe and Nandi, J., 1941, 70) can also be employed in the case of diselenides, an extra atomic proportion of selenium being used.

The following crystalline derivatives of the dialkyl monoselenides (Me, Et, and *n*-Pr) have been prepared: *dimethylselenetine bromide*, $\text{Me}_2\text{Se}(\text{Br})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, *diethyl selenide dibromide* (previously described as an oil), and *di-n-propyl selenide dibromide*.

Dialkylselenones have not been described, although methyl- and ethyl- β -naphthylselenones have been obtained by Loevenich, Fremdling, and Föhr (*Ber.*, 1929, **62**, 2856). The action of hydrogen peroxide on dimethyl selenide gave no selenone but either methaneseleninic acid (with loss of a methyl group) or a mixture of this acid with dimethyl selenide dihydroxide, $(\text{CH}_3)_2\text{Se}(\text{OH})_2$, or dimethyl selenoxide, $(\text{CH}_3)_2\text{SeO}$. The mixture was identified by its behaviour with hydrobromic acid, giving methylselenium tribromide and dimethyl selenide. Similar results were obtained in the tellurium series by Balfe, Chaplin, and Phillips (*loc. cit.*), who state that *n*-butyl telluride on oxidation with air or neutral hydrogen peroxide gives double compounds of di-*n*-butyl telluroxide and *n*-butyltellurinic acid, *e.g.*, $2\text{TeBu}_2\text{O}, \text{BuTeO}\cdot\text{OH}$, and also butyric acid. They regard the last two compounds as oxidation products of *n*-butyltellurol and *n*-butaldehyde arising thus: $(\text{C}_4\text{H}_9)_2\text{TeO} = \text{C}_3\text{H}_7\cdot\text{CHO} + \text{C}_4\text{H}_9\cdot\text{TeH}$. They also draw attention to similar decompositions of alkyl selenoxides and sulphoxides (see also Challenger and Rawlings, J., 1937, 870).

This formation of the dihydroxide or selenoxide suggested an examination of the action of aqueous silver oxide on R_2SeBr_2 . The diethyl and di-*n*-propyl dibromides gave the slightly impure silver salts of ethaneseleninic acid and propane-1-seleninic acid. The dimethyl derivative gave the dihydroxide or selenoxide, identified as before, and a trace of an acidic product, probably the seleninic acid. The product altered in *m. p.* on keeping in a desiccator and may then have contained complex compounds analogous to the tellurium derivatives described by Balfe and his co-workers (*loc. cit.*). On heating, both specimens decomposed, giving formaldehyde, presumably thus: $(\text{CH}_3)_2\text{SeO} = \text{CH}_2\text{O} + \text{CH}_3\cdot\text{SeH}$ (see above). Formaldehyde is also produced on heating methaneseleninic acid, the reaction probably proceeding thus:



When methane-, ethane-, and propane-1-seleninic acids or their hydrogen nitrates are carefully oxidised with potassium permanganate in almost neutral solution, the potassium salts of the alkaneselenonic acids are obtained. Alkaneselenonic acids have not previously been described, although certain aromatic analogues have been prepared by a similar method (Pyman, J., 1919, **115**, 166) and also by the action of selenic acid on aromatic hydrocarbons (Doughty, *Amer. Chem. J.*, 1909, **41**, 326; Anschütz, Kallen, and Riepenkröger, *Ber.*, 1919, **52**, 1860; Anschütz and Teutenberg, *Ber.*, 1924, **57**, 1018). The salts of the alkaneselenonic acids readily eliminate selenious acid on heating with dilute acid or alkali. Like their aromatic analogues they explode slightly on heating. Potassium ethaneselenonate is gradually decomposed by warm aqueous permanganate, evolving some acetaldehyde; the methyl derivative is stable under these conditions.

Mr. J. W. Fletcher (private communication) found that, on oxidation with permanganate, dimethyl selenide yields methaneseleninic acid, methaneselenonic acid and selenious acid. These were isolated as the free acid, the potassium and the barium salt respectively and analysed.

The conversion of diselenides into selenothiols on reductive fission with sodium and alcohol was employed in the preparation of methyl ethyl and methyl *n*-propyl selenides. These were conveniently obtained by direct treatment of the alkaline solution of the selenothiol with the required alkyl halides. They were characterised as the mercurichlorides.

The dialkyl disulphides undergo fission with mercuric chloride, yielding, in the first instance, $\text{R}\cdot\text{S}\cdot\text{HgCl}$ and $\text{R}\cdot\text{S}\cdot\text{Cl}$, but are stable to mercuric cyanide (Challenger and Rawlings, J., 1937, 868). Both these mercuric salts, however, cause fission of the dialkyl diselenides. The products have not been so carefully examined as in the case of the disulphides, but with dimethyl and diethyl diselenides an alkyl selenocyanate is formed; the other products appear to be cyanomercurymethylselenothiol, $\text{CH}_3\cdot\text{Se}\cdot\text{HgCN}$, and dimercury ethylselenothiol $(\text{C}_2\text{H}_5\cdot\text{Se})_2\text{Hg}$.

With dimethyl diselenide and mercuric chloride the insoluble product appears to be a mixture of $\text{CH}_3\cdot\text{Se}\cdot\text{HgCl}, \text{HgCl}_2$ with a little $\text{CH}_3\cdot\text{Se}\cdot\text{HgCl}$ (compare Challenger and Rawlings, *loc. cit.*). The aromatic diselenides also undergo fission with bromine, giving arylselenium bromide, $\text{R}\cdot\text{SeBr}$, and tribromide, $\text{R}\cdot\text{SeBr}_3$ (Behaghel and Seibert, *Ber.*, 1932, **65**, 812).

Although selenious acid does not appear to give rise to compounds derived from the form $\text{H}\cdot\text{SeO}_2\cdot\text{H}$ (Strecker and Daniels, *Annalen*, 1928, **462**, 186), β -naphthaleneseleninic acid gives both seleninic esters and selenones according to the particular reagent employed (Loevenich, Fremdling, and Föhr, *Ber.*, 1929, **62**, 2856). Neither ester nor selenone is produced from sodium methaneseleninate and methyl sulphate or from the sodium or silver salt with methyl iodide. Iodine is liberated in the latter case, probably thus: (a) $\text{CH}_3\cdot\text{SeO}_2\text{Na} + \text{CH}_3\text{I} + \text{HOH} = \text{CH}_3\cdot\text{SeO}_2\text{H} + \text{NaI} + \text{CH}_3\cdot\text{OH}$; (b) $2\text{CH}_3\cdot\text{SeO}_2\text{H} + 6\text{NaI} + 2\text{H}_2\text{O} = (\text{CH}_3)_2\text{Se}_2 + 6\text{NaOH} + 3\text{I}_2$.

EXPERIMENTAL.

Preparation of Alkyl Selenides.—A mixture of sodium formaldehydesulphoxylate ("rongalite") (90 g.; 0.76 mol.), sodium hydroxide (70 g.; 1.75 mols.), powdered selenium (25 g.; 0.32 mol.), and water (300 c.c.) was warmed to about

50° and slowly treated with the alkyl iodide (Me = 41.5 c.c., Et = 54 c.c., and *n*-Pr = 67.5 c.c.; 0.32 mol. in each case). The reaction was vigorous with methyl iodide and in all cases was completed by warming under reflux for 1—3 hours. If addition of the methyl and ethyl iodides was too rapid, the yield of selenide was diminished owing to the formation of the trialkylselenium iodide, which separated on the sides of the flask. Dimethyl selenide was removed on the water-bath; the homologues were separated on addition of water and extraction with ligroin. Distillation yielded pure products having the b. p. given in the literature. The yields of the methyl and *n*-propyl selenides were 88 and 54%. That of the ethyl compound was of the same order. The method is a very convenient one.

Dimethylselenetine bromide was prepared from dimethyl selenide and ethyl bromoacetate and after crystallisation from alcohol-ether melted at 90° (decomp.) (Found: Br, 29.0. $C_6H_{13}O_2BrSe$ requires Br, 29.0%).

Diethyl selenide dibromide was obtained from the selenide and the calculated amount of bromine, both in cooled carbon tetrachloride. The solvent was removed under diminished pressure, and the residue cooled, giving brown plates, in theoretical yield, m. p. 37° (decomp.). They were not recrystallised (Found: Br, 54.0. Calc. for $C_4H_{10}Br_2Se$: Br, 53.9%). This compound is stated to be an oil. After 6 months in a closed tube decomposition to black selenium, m. p. 217°, had occurred.

Di-n-propyl selenide dibromide. The selenide (0.1 mol.) and bromine (0.2 mol.) in carbon tetrachloride gave a red oil which soon solidified to orange crystals, m. p. 50°; yield, theoretical. They were recrystallised from hot dilute hydrobromic acid (Found: Br, 49.1. $C_6H_{14}Br_2Se$ requires Br, 49.2%). The dibromide is insoluble in cold water but soluble in hot, giving a colourless solution. It is very soluble in ether, alcohol, and acetone. After 6 months in a closed tube it had almost completely decomposed to black selenium, m. p. 217°, and a red liquid smelling like *n*-propyl bromide.

Oxidation of Dimethyl Selenide with Hydrogen Peroxide.—"Perhydrol" and the cooled selenide were not miscible, but on standing the temperature rose and a vigorous reaction occurred, giving a homogeneous solution. After being heated at 100° for 30 minutes, this was evaporated at 16 mm. The residue solidified in a desiccator overnight, giving white needles, m. p. 131°, unchanged on recrystallisation from chloroform (Found: C, 9.8; H, 3.2; equiv., by titration with NaOH, 128. Calc. for CH_3O_2Se : C, 9.5; H, 3.2%; equiv., 127. Calc. for CH_3O_2Se : C, 8.4; H, 2.8%). Its identification as methaneseleninic acid was confirmed by the production of an odour of methyl hydrogen selenide on reduction with zinc and hydrochloric acid, and by the formation of a salt with benzenesulphonic acid, m. p. 150° (decomp.); Backer and van Dam (*Rec. Trav. chim.*, 1935, **54**, 535) give m. p. 150° (decomp.). When the seleninic acid was gently warmed, formaldehyde was evolved; it was identified by its odour and by the formation of the 2:4-dinitrophenylhydrazone, m. p. 161°, and mixed m. p. 162—165° with an authentic specimen of m. p. 165°. A yellow oil, turning red and then volatilising, giving a residue of red selenium and a sublimate of white needles, probably selenium dioxide, was also produced. A concentrated aqueous solution of the seleninic acid gave with hydrobromic acid hygroscopic orange crystals, m. p. 75° (decomp.). These could not be recrystallised from water or hydrobromic acid and depressed the m. p. of dimethyl selenide dibromide (85°) to 65°. Titration showed them to be slightly impure *methylselenium tribromide* (Found: Br, 70.0. CH_3Br_3Se requires Br, 71.9%). The seleninic acid was also obtained from dimethyl selenide with perhydrol in glacial acetic acid. 90% Hydrogen peroxide being used without a solvent, crystals of methaneseleninic acid separated from the concentrated reaction mixture. Removal of these and treatment of the residue with hydrobromic acid gave (a) yellow needles, m. p. and mixed m. p. 86° (decomp.) with dimethyl selenide dibromide (m. p. 90° decomp.), and (b) methylselenium tribromide, m. p. 75° (decomp.).

Dimethyl Selenide Dibromide and Silver Oxide.—The dibromide was ground with water and a very slight excess of silver oxide. The clear neutral filtrate was evaporated at ordinary temperature under diminished pressure and left over sulphuric acid in a vacuum desiccator for 7 days; the very deliquescent residue (A) then solidified, m. p. 86° in a sealed tube. This gave formaldehyde on heating and was distinctly acid to litmus. With hydrobromic acid it regenerated the dibromide, m. p. and mixed m. p. 85°. On keeping over sulphuric acid for 3 months the m. p. of A rose to 135°, and 136° (decomp., giving formaldehyde and a red oil) on recrystallisation from alcohol. Mixed m. p. with methaneseleninic acid (m. p. 127°) was 105°. With hydrobromic acid the dibromide ($CH_3)_2SeBr_2$ was regenerated. When the dibromide was treated with a large excess of silver oxide in water, and the alkaline filtrate shaken with nitric acid and evaporated as before, neutral white crystals, m. p. 127°, containing neither silver nor halogen were obtained. These products were not further examined (see p. 571).

Diethyl Selenide Dibromide and Silver Oxide.—This reaction proceeds differently from that with the dimethyl derivative. Excess of aqueous silver oxide gave a silver salt on evaporation at 100°/15 mm., which appeared to be slightly impure silver ethaneseleninate (Found: equiv., 255. Calc. for $C_2H_5O_2AgSe$: equiv., 248). An ethyl group was therefore lost during the operation.

Di-n-propyl Selenide Dibromide and Silver Oxide.—Almost twice the amount of silver oxide necessary to remove all the bromine was required and the aqueous filtrate was evaporated at 50°/16 mm. A brownish powder separated which appeared to be slightly impure silver *n*-propaneseleninate (Found: equiv., 252. Calc. for $C_3H_7O_2AgSe$: equiv., 260). The aqueous filtrate had a sweet ester-like odour, possibly due to *n*-propyl propionate arising from the action of silver oxide on propaldehyde.

Oxidation of Alkaneseleninic Acids.—(a) *Potassium methaneselenonate*. Methaneseleninic acid (5.9 g.) and potassium hydroxide (0.83 g.; 0.015 mol.) were dissolved in water (15 c.c.) and slowly treated during 10 minutes with potassium permanganate (4.8 g.; 0.03 mol.) in water (90 c.c.). The quantities were calculated so that the solution should be almost neutral on completion of the oxidation. The mixture became warm and was finally exactly neutralised with potassium hydroxide and filtered. Evaporation under diminished pressure at about 40° (an essential precaution in all cases) left a white residue (6—7 g.), which was recrystallised from alcohol, giving shining white crystals. This and the other potassium salts of the seleninic acids were analysed by heating with hydrochloric acid under reflux for 3 hrs. (an alcohol is then eliminated, leaving selenious acid), diluting the solution with water, treating it with sulphur dioxide and hydrazine hydrate, and weighing the precipitated selenium (Found: Se, 43.3. CH_3O_2KSe requires Se, 43.6%). A similar decomposition occurs with hot baryta water, giving barium selenite. In the cold no trace of precipitate was obtained with baryta, indicating the absence of selenite and selenate. The absence of potassium alkaneseleninate was shown by the following comparative tests:

Reagent.	$CH_3^*SeO_2H$.	$CH_3^*SeO_3K$.
Warm hydrochloric acid	Decided odour of alkyl Se compound. No precipitate of Se.	Decomposition with effervescence. No odour. No precipitate of Se.
NaHSO ₃	Yellow oil, odour of CH_3^*SeH . No Se.	No odour. No Se.
NaHSO ₃ + HCl	As for NaHSO ₃ .	No odour. Se precipitated.
Zinc and acetic acid	Yellow oil, odour of CH_3^*SeH . No Se.	No odour. Se precipitated.

(b) *Potassium ethaneselenonate* was similarly prepared from ethaneseleninic acid (2.9 g.) and potassium hydroxide (0.38 g.), in water (8 c.c.), and potassium permanganate (2.15 g.) in water (45 c.c.). An odour of acetaldehyde was noticed towards the conclusion of the oxidation. The mixture was kept at room temperature for 2 hours and treated

as in (a). Crystallisation from alcohol containing a drop of water gave shining white plates free from selenite, selenate or ethaneseleninate (Found: Se, 40.0. $C_2H_5O_3KSe$ requires Se, 40.5%). The yield was not so good as in (a) owing to the more easy oxidation of the ethyl group (compare p. 572). Thus *potassium ethaneselenonate* is very sensitive to excess of potassium permanganate, whereas the corresponding methyl compound is stable to the warm reagent. The oxidation of ethaneseleninic acid hydrogen nitrate ($C_2H_5 \cdot SeO_2H \cdot HNO_3$) with potassium permanganate and an extra equivalent of potassium hydroxide also gave pure potassium ethaneselenonate on extraction of the product with alcohol.

(c) *Potassium propane-1-selenonate* was similarly prepared from propane-1-seleninic acid hydrogen nitrate (12.1 g.), potassium hydroxide (4.15 g.) in water (30 c.c.) and potassium permanganate (5.8 g.) in water (120 c.c.). The salt formed shining white plates from alcohol, which were dried at 100°/15 mm. for 3 hrs. (Found: Se, 38.0. $C_3H_7O_3KSe$ requires Se, 37.6%). Selenate, selenite, and alkaneseleninate were absent. Yield, 40%.

As the potassium alkylselenonates were intended as substrates for the mould *Scopulariopsis brevicaulis*, it was essential to prove that they actually had the structure assigned to them, and that they were not, in fact, potassium alkyl selenates $RO \cdot SeO_2 \cdot OK$ or potassium alkyl selenites $RO \cdot SeO \cdot OK$. Their preparation from the diselenides through the seleninic acids seemed conclusive evidence on this point, but further confirmation was sought. The presence of a C-Se link in each compound was shown by the production of an intense odour of an alkylselenothiol on addition of aluminium amalgam to an aqueous solution of the salt. This reaction is also given by the corresponding potassium alkaneseleninates $R \cdot SeO_2K$. Their absence was, however, demonstrated by the sodium hydrogen sulphite test (see above), which gave no odour of a selenothiol. After 2 years the three potassium alkaneselenonates all gave a precipitate with barium hydroxide solution, which was soluble in dilute hydrochloric acid, indicating the presence of some selenite and consequent partial decomposition. This was only slight in the case of the methyl and the ethyl derivative and more pronounced with the propyl compound. Recrystallisation of the potassium propane-1-selenonate from alcohol removed the impurity and after 6 weeks in a closed tube the specimen was still free from selenite and also from seleninate, although a faint odour of an alkyl selenide or selenothiol could be detected on opening the tube.

Action of Methyl Iodide and of Methyl Sulphate on Salts of Methaneseleninic Acid.—The seleninic acid (7.6 g.) was exactly neutralised with sodium carbonate and evaporated at 50°/10 mm., giving a viscous residue which when kept in a vacuum desiccator over sulphuric acid gave long deliquescent needles of the sodium salt. These (8.9 g.; 0.06 mol.) were dissolved in hot alcohol, cooled, and treated with methyl iodide (8.5 g.; 0.072 mol.). No apparent reaction took place, so the mixture was heated for 4 hrs. at 100°; it then gradually darkened. Removal of solvent under diminished pressure left a residue with an unpleasant odour, containing free iodine. Removal of this with sodium thiosulphate left a dark oil with an odour of dimethyl diselenide.

Aqueous methaneseleninic acid was warmed with silver oxide, needles of the silver salt separating from the filtrate. These were left in methyl alcohol with a slight excess of methyl iodide for 20 hrs. Evaporation of the filtrate gave methaneseleninic acid, m. p. and mixed m. p. 134° (decomp.). The residue of silver iodide contained no selenium compound.

Methaneseleninic acid in excess of sodium hydroxide solution was shaken with the calculated quantity of methyl sulphate and left till the mixture was homogeneous. Extraction with chloroform removed nothing, before or after heating under reflux, though an unpleasant odour was noticed. Unchanged seleninic acid was recovered on evaporation with dilute nitric acid and extraction with ethyl acetate.

Preparation of Dialkyl Diselenides.—The methyl, ethyl, and *n*-propyl derivatives were very conveniently obtained by gradual addition of the calculated quantity of methyl sulphate, ethyl sulphate, and *n*-propyl iodide to a solution of two atomic proportions of selenium in the exact amounts of sodium hydroxide and sodium formaldehydesulphoxylate necessary to form sodium diselenide. Details are given for dimethyl diselenide. Selenium (32 g.) was completely dissolved in a mixture of sodium hydroxide (16 g.) and sodium formaldehydesulphoxylate (25 g.) in water (250 c.c.). Methyl sulphate (22 c.c.) was added and after heating for 1 hr. the reddish-brown colour had almost completely disappeared and a heavy oil separated. This was extracted with chloroform, dried over sodium sulphate, and fractionated, giving a little dimethyl selenide and 22 g. of the diselenide as an orange oil, b. p. 153°; yield, 60%. This was fractionated three times, the b. p. remaining constant at 153°/16 mm. Van Dam gives b. p. 155–157°/21 mm.

Diethyl diselenide was obtained in 60% yield and boiled constantly at 85°/21 mm. Rathke (*Annalen*, 1869, **152**, 216) gives 77–78°/16 mm. Di-*n*-propyl diselenide (50% yield) had constant b. p. 105°/11 mm. Tschugaeff (*Ber.*, 1909, **42**, 49) gives 99°/13 mm.

Fission of Dimethyl Diselenide.—(a) *By mercuric cyanide.* When the diselenide was added to excess of 5% aqueous mercuric cyanide, a yellow solid separated which contained nitrogen. This could not be crystallised from any solvent owing to its insolubility. It decomposed at 101° with frothing and turned black. No odour of an alkyl selenium compound was observed on warming with hydrochloric acid or sodium hydroxide. The filtrate from this precipitate was extracted with ether, yielding a few drops of oil, b. p. ca. 150°, having a characteristic odour. Direct comparison with methyl selenocyanate, b. p. 155° (Stolte, *Ber.*, 1886, **19**, 1577, gives 158°), showed the odours to be identical. When the fission was repeated in aqueous alcoholic solution, 1.2 g. of dimethyl diselenide being used, 1.3 g. of the yellow precipitate, presumably $CH_3 \cdot Se \cdot HgCN$, was obtained. Calc., 2.0 g. On keeping, it darkened, finally giving an odourless black powder containing mercury and selenium.

(b) *Fission by acidified mercuric chloride.* Addition of dimethyl diselenide alone or in alcohol to Biginelli's solution (mercuric chloride, 10 g.; water, 80 c.c.; hydrochloric acid, 20 c.c.) gave yellow insoluble needles, m. p. 123° (Found: Cl, 16.4. $CH_3SeClHg \cdot HgCl_2$ requires Cl, 17.7%). The product probably contained some $CH_3 \cdot Se \cdot HgCl$.

When dimethyl diselenide was aerated first through mercuric cyanide and then through Biginelli's solution, it was completely retained by the cyanide and no trace of precipitate formed in the acid mercuric chloride, indicating the absence of monoselenide from the specimen.

Di-*n*-propyl diselenide, when aerated into mercuric cyanide or Biginelli's solution for several hours, gave no precipitate. Direct addition to alcoholic mercuric cyanide slowly gave a yellow solid, m. p. 138° (decomp.). It was not further examined.

Methyl Ethyl Selenide Mercurichlorides.—Dimethyl diselenide was dissolved in alcohol and treated with just over two atomic proportions of sodium, giving an orange solution and a black precipitate. On addition of ethyl iodide (2 mols.) reaction occurred at once. The clear yellow solution was refluxed for 30 mins., water added, and the mixture distilled in steam. The yellow distillate contained a little unchanged diselenide and, judging from the odour, a monoselenide also. Volatile matter was removed in an air stream through mercuric cyanide (to remove dimethyl diselenide) into Biginelli's solution, where white needles formed, m. p. 98°, decomposing at 140°. After drying in a vacuum, these melted at 100° and decomposed as before. On crystallisation from 3% aqueous mercuric chloride the m. p. was 140° (decomp.) (probably a higher mercurichloride) and from 50% alcohol 100°. This product was dried over sulphuric acid (Found: Hg, 51.8; Cl, 18.0. $C_3H_7O_2HgSe$ requires Hg, 52.3; Cl, 18.0%).

The preparation was repeated, diethyl diselenide, alcohol, sodium, and methyl iodide being used. Aspiration through Biginelli's solution as before gave the same product, m. p. and mixed m. p. 100°. $(CH_3)_2Se \cdot HgCl_2$ melts at 153° (decomp.), and $(C_2H_5)_2Se \cdot HgCl_2$ at 93°. An equimolecular mixture had m. p. 80–87°.

Although the methyl ethyl selenide mercurichloride, m. p. 140°, had been obtained by two different methods, the

experiments were on a very small scale. It therefore appeared desirable to confirm these results, especially in view of the formation of a black precipitate which may have been selenium, capable of giving rise to some sodium selenide and hence to dimethyl selenide. The following experiment, however, fully confirmed the earlier ones.

Dimethyl diselenide (19.4 g.; 1 mol.) in dry ether (40 c.c.) was added to sodium shavings (15 g.; 6 atoms) covered with dry ether (160 c.c.), in a flask cooled in water and carrying a reflux condenser connected to wash-bottles containing mercuric chloride to prevent escape of vapours. Alcohol (70 c.c.) was slowly added, giving a steady effervescence and a red turbidity. A slow stream of nitrogen was passed through to avoid oxidation of the sodium methylselenothiol. Ethyl bromide (80 g.; 6 mols.) was slowly added and also a further 20 c.c. of alcohol to ensure removal of all the sodium. Sodium bromide separated and the red colour disappeared entirely. Next day the mixture was refluxed for an hour, and most of the ether then removed with a column (Ether-Selenide Fraction I). On continuing distillation on the steam-bath without a column Fraction II was obtained. Addition of water to the pasty residue gave an oil. This was extracted with ether, and the dried extract repeatedly fractionated, finally yielding Fraction III.

Test portions of the three fractions were separately treated with aqueous mercuric chloride, and the resulting mercurichlorides carefully examined by repeated recrystallisation from (a) alcohol and (b) aqueous mercuric chloride. Determinations of m. p. and mixed m. p. showed them to be essentially the same. From (a) the m. p. was 100° and from (b) 141.5° (decomp.) in close agreement with the results obtained in the small-scale experiments.

As a further check the three ether-selenide fractions were mixed and added to excess of aqueous mercuric chloride. The resulting solid W (as in all these experiments) was initially a mixture of the two mercurichlorides of methyl ethyl selenide. Repeated recrystallisation of a portion from aqueous mercuric chloride gave a homogeneous product, m. p. 141.5° (decomp.).

Finally the bulk of the mixture W (50 g.) was decomposed with excess of aqueous sodium hydroxide, and the liberated methyl ethyl selenide distilled from a steam-bath and dried over calcium chloride. Repeated distillation showed the product to be homogeneous, b. p. 86—87°. The slight amounts remaining in the flask each time were united and redistilled, b. p. 86—90°. Methyl ethyl selenide boils at 86° (Tschugaeff, *loc. cit.*). A few drops when added to excess of mercuric chloride gave a product, m. p. 141.5° (decomp.) (Found: Cl, 21.7. $\text{CH}_3\text{SeC}_2\text{H}_5, 2\text{HgCl}_2$ requires Cl, 21.4%). This convenient method obviates the use of hydrogen selenide and the isolation of the selenothiol. *Methyl ethyl selenide dimercurichloride* is stable in air, but the monomercurichloride gradually loses dimethyl selenide with formation of some dimercurichloride and consequent rise in m. p. When decomposed with sodium hydroxide, the resulting yellow mercuric oxide is not reduced by the selenide even at 100°. Alkyl selenides differ in this respect from trialkylarsines (Challenger, Higginbottom, and Ellis, J., 1933, 99) and from dimethyl telluride (Bird and Challenger, J., 1939, 166).

Methyl n-Propyl Selenide Mercurichloride.—The preparation was analogous to that of the methyl ethyl compound. Both dimethyl diselenide and di-*n*-propyl diselenide were used as starting points and the mercurichloride had the same m. p. (87°) in each case. On recrystallisation from alcohol the m. p. was 88° (Found: Hg, 49.2; Cl, 17.8. $\text{C}_4\text{H}_{10}\text{Cl}_2\text{HgSe}$ requires Hg, 49.2; Cl, 17.5%). With neutral mercuric chloride as absorbent the product melted at 160° (decomp.) but was not analysed. *Di-n-propyl selenide mercurichloride*, whether formed from its ingredients in aqueous alcoholic solution or in Biginelli's solution, melts at 93—94° after recrystallisation from alcohol (Found: Hg, 45.1. $\text{C}_6\text{H}_{14}\text{Cl}_2\text{HgSe}$ requires Hg, 45.8%). In admixture with methyl *n*-propyl selenide mercurichloride the m. p. was 70—85°.

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