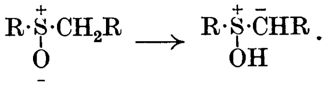
CCXCIX.—*The Quadrivalency of Selenium. Part III. The Instability of the Compounds of Quadrivalent Selenium derived from Phenyl Methyl and Phenyl Ethyl Selenides and Phenyl- and* p-*Tolyl-selenoglycollic Acids.*

By Owen Kempster Edwards, Wilson Robinson Gaythwaite, Joseph Kenyon, and Henry Phillips.

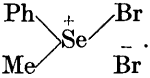
Owing to their instability, much difficulty has been experienced in the preparation of selenoxides containing an alkyl group attached to the selenium atom. Such selenoxides have been found to decompose on heating mainly as indicated by the equation $\mathrm{SeRO{\cdot}CH_2R = SeRH + O{:}CHR}$. They differ widely in this respect from purely aromatic selenoxides, such as 4-acetamidodiphenyl selenoxide, which, as described in the preceding communication, decomposes on heating into the corresponding selenide and oxygen.

Sulphoxides containing an alkyl group attached to the sulphur atom are known to undergo a similar change. For example, Fromm and Achert (*Ber.*, 1903, **36**, 534) obtained benzaldehyde by heating benzyl sulphoxide; Smythe (J., 1909, **95**, 349) showed that during the interaction of this sulphoxide with hydrogen chloride in various solvents, benzaldehyde, benzyl mercaptan, dibenzyl disulphide, and benzyl chloride were produced. Similarly, Fichter and Sjöstedt (*Ber.*, 1910, **43**, 3422) and Fichter and Wenk (*Ber.*, 1912, **45**, 1373) showed that the controlled electrochemical oxidation of phenyl ethyl sulphide yielded phenyl mercaptan and acetaldehyde. Pummerer (*Ber.*, 1909, **42**, 2282 ; 1910, **43**, 1404), who investigated the conversion of phenyl- and *p*-tolyl-sulphoxyacetic acids into glyoxylic acid and the corresponding aromatic thiols (by the agency of heat or traces of mineral acids), was led to suggest, as the underlying cause, the tendency on the part of such sulphoxides to assume an isomeric form by a process analogous to the keto-enol change. On the electronic conceptions of valency, Pummerer's formulation of the initial step in the decomposition could be written

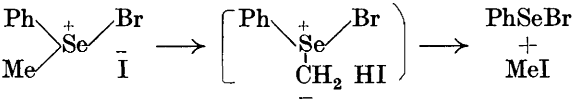


$$\mathrm{R{\cdot}\overset{+}{\underset{\underset{-}{O}}{S}}{\cdot}CH_2R} \longrightarrow \mathrm{R{\cdot}\overset{+}{\underset{OH}{S}}{\cdot}\overset{-}{C}HR}.$$

Since we find that selenoxides of analogous constitution to the sulphoxides mentioned decompose in a similar fashion, it is possible that selenoxides also may undergo an isomeric change of this nature. The following compounds of quadrivalent selenium have therefore been investigated in order to obtain evidence as to whether the migration of hydrogen is an initial phase of their decomposition.

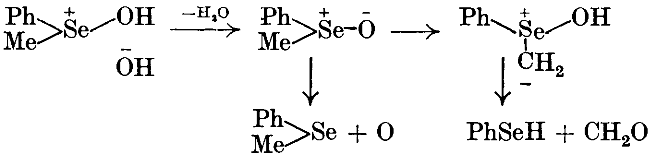
Phenyl methyl selenide dibromide, prepared by the addition of bromide to phenyl methyl selenide, is a well-defined, bright red crystalline substance. On heating at about 100° it decomposed quantitatively into methyl bromide and bromoselenobenzene. When triturated at 40° with a concentrated solution of potassium iodide, the dibromide was converted into the *di-iodide*; if, however, the dibromide was treated with a cold solution of potassium iodide of the same concentration, a *bromo-iodide* was obtained in theoretical yield. This compound, on heating, decomposed quantitatively to give methyl iodide and bromoselenobenzene. These results clearly indicate that the bromine atoms of phenyl methyl selenide dibromide are not linked in the same manner to the selenium atom, and hence agree with a formula such as  $\begin{matrix}\mathrm{Ph} & & \mathrm{Br} \\ & >\overset{+}{\mathrm{Se}}< & - \\ \mathrm{Me} & & \mathrm{Br}\end{matrix}$.

The facility with which the dibromide and the bromo-iodide decompose into alkyl halogen compounds and bromoselenobenzene is most marked, and that the presence of the methyl group is in some way responsible is evident, since diphenyl selenide dibromide (Krafft and Lyons, *Ber.*, 1894, **27**, 1761) has been found to decompose into bromodiphenyl selenide and hydrobromic acid, whilst 4-acetamidodiphenyl selenide dibromide yields 3 : 5-(?)dibromo-4-acetamidodiphenyl selenide and hydrobromic acid (preceding communication). The mode of decomposition of phenyl methyl selenide bromo-iodide is therefore not inconsistent with the view that such decompositions pass through a preliminary phase, as indicated below, which involves the loss of a proton by the methyl group and causes this group to become less firmly attached to the selenium atom.



Phenyl ethyl selenide dibromide was also found to decompose quantitatively when heated at 130° into ethyl bromide and bromoselenobenzene.

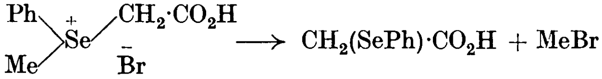
Phenyl methyl selenide dihydroxide, prepared by treating a solution of the dibromide in water with silver oxide, and concentrating the filtrate in a vacuum, was obtained as a viscous oil, which, when heated at 100°/15 mm. or at 170°/760 mm., decomposed yielding phenyl methyl selenide, diphenyl diselenide, and formaldehyde. The phenyl methyl selenide may have been produced by the reduction of the dihydroxide or selenoxide by the other products of the decomposition. The formation of formaldehyde is in agreement with the view that phenyl methyl selenoxide may exist in two isomeric forms which, being unstable, decompose thus :



Unsuccessful attempts were made under various experimental conditions to cause phenyl methyl selenide dihydroxide to lose water and yield a selenoxide. These experiments led to the conclusion that the selenoxide, when formed, immediately decomposed, and they were therefore abandoned.

Phenyl ethyl selenide dihydroxide, prepared from the dibromide by similar methods, was found to be less stable than its lower homologue, and decomposed yielding mainly diphenyl diselenide, even when left in a vacuum desiccator containing sulphuric acid.

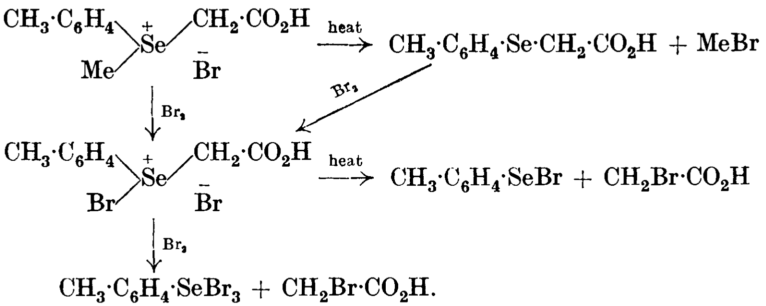
Phenyl- and p-*Tolyl-methylselenetine Bromides.*—Phenylmethylselenetine bromide, prepared by the method of Pope and Neville (J., 1902, **81**, 1552), was found to decompose smoothly and quantitatively at its m. p. into methyl bromide and phenylselenoglycollic acid :



$$\begin{matrix}\mathrm{Ph} & & \mathrm{CH_2{\cdot}CO_2H}\\ & \overset{+}{\mathrm{Se}} & \\ \mathrm{Me} & & \overset{-}{\mathrm{Br}}\end{matrix} \longrightarrow \mathrm{CH_2(SePh){\cdot}CO_2H + MeBr}$$

Similarly, *phenylselenoglycollic acid dibromide* decomposed when heated, yielding bromoselenobenzene and bromoacetic acid. Attempts were made to prepare phenylethylselenetine bromide by the interaction of phenyl ethyl selenide and bromoacetic acid; phenylselenoglycollic acid was, however, the only product isolated, owing, presumably, to the ease with which the selenetine bromide produced decomposed.

p-*Tolylmethylselenetine bromide* was also prepared from *p*-tolyl methyl selenide and bromoacetic acid. On heating, it softened at 85—88°, turned more definitely crystalline, and finally became molten at 96—97°, the m. p. of *p*-tolylselenoglycollic acid (Morgan and Porritt, J., 1925, **127**, 1758). When treated with a molecular proportion of bromine in cold carbon tetrachloride solution, *p*-tolylmethylselenetine bromide was converted into *p*-tolylselenoglycollic acid dibromide which, on heating, decomposed smoothly into *p*-bromoselenotoluene and bromoacetic acid. The replacement of the methyl group of *p*-tolylmethylselenetine bromide by means of bromine occurs with great readiness. This possibly explains why we were unable to obtain *p*-tolylselenoglycollic acid tetrabromide by the action of excess of bromine on *p*-tolylselenoglycollic acid, as described by Morgan and Porritt (*loc. cit.*). We found, in agreement with the results of our other experiments, that the dibromide produced as an initial stage of the reaction was converted by the excess of bromine into *p*-bromoselenotoluene dibromide and bromoacetic acid. The results of the experiments with these compounds can be summarised as follows :



All the decomposition reactions which have been described support the contention that the withdrawal of aliphatic groups from their combination with quadrivalent selenium may be facilitated by their ability to provide a proton. The most striking example is the decomposition of *p*-tolylselenoglycollic acid dibromide, which does not decompose into *p*-tolylselenoglycollic acid and bromine, as might be expected (compare Morgan and Porritt, *loc. cit.*), but into bromoselenotoluene and bromoacetic acid.

EXPERIMENTAL.

The Action of Heat on Phenylmethylselenetine Bromide.—Phenylmethylselenetine bromide was prepared by the method of Pope and Neville (*loc. cit.*). Equimolecular amounts of phenyl methyl selenide (8·6 g.) and bromoacetic acid (7·0 g.) were gently warmed until molten and allowed to stand over-night; dry ether was then added to the reaction mixture from which a mass of crystals had separated. The white, additive compound (7·6 g.) removed by filtration had m. p. 110—111°, with evolution of a gas. After recrystallisation from a mixture of alcohol and ether, the phenylmethylselenetine bromide had m. p. 111° as recorded by Pope and Neville.

0·4665 G. of this bromide was heated at about 110° until the evolution of gas had ceased; the gas was passed into an aqueous-alcoholic solution of silver nitrate and produced a copious precipitate of silver bromide. The residual product when cold weighed 0·3256 g., the loss being 30·2% (Calc. for loss of CH_3Br, 30·6%). The residual product was an acid (Found: equiv., 230. Phenylselenoglycollic acid, $C_6H_5{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$, requires equiv., 215). The acid thus obtained in another experiment was seeded with phenylselenoglycollic acid and set to a mass of colourless crystals, m. p. 36—37°, either alone or when mixed with phenylselenoglycollic acid prepared by the method of Morgan and Porritt (*loc. cit.*). (Although the acid was obtained as described by these authors, yet the physical constants recorded by them, b. p. 160°/750 mm., m. p.

40°, are considerably different from those now found, *viz.*, b. p. 197—198°/10 mm., m. p. 36—37°.)

It was not found possible to synthesise phenylmethylselenetine bromide from phenylselenoglycollic acid and methyl bromide. A dry ethereal solution of these two substances was kept in a stoppered bottle for 50 days, but did not deposit crystals of the insoluble selenetine bromide. Further, phenylmethylselenetine bromide was heated in a sealed tube at 110° until completely molten; after 24 hours, the tube (the contents of which were still fluid) was opened and found to be under considerable pressure, which was due to the presence of methyl bromide, since the still molten contents of the tube crystallised when inoculated with a crystal of phenylselenoglycollic acid.

Phenylselenoglycollic acid dibromide was prepared by the addition of a solution of bromine (8 g.) in warm carbon tetrachloride (50 c.c.) to a hot solution of phenylselenoglycollic acid (10·75 g.) in carbon tetrachloride (500 c.c.). The additive compound (18·3 g.; yield 97%) separated in very small, yellow, ill-defined needles, which melted at 126° to a deep red liquid (Found : Br, 42·3. $C_8H_8O_2Br_2Se$ requires Br, 42·7%), and were almost insoluble in carbon tetrachloride, chloroform, benzene, or carbon disulphide; they dissolved in about 10 times their weight of hot glacial acetic acid, but on cooling, the solution deposited deep red crystals of bromoselenobenzene, m. p. 61°, in almost theoretical amount (Found : Br, 33·9. Calc. : Br, 33·9%).

Action of Heat on Phenylselenoglycollic Acid Dibromide.—(*a*) When this dibromide (3·7 g.) was heated, the products of decomposition distilled at 100—102°/12 mm. and set to a brownish-red, crystalline mass. When about two-thirds of the material had distilled, the temperature began to rise and the distillation was stopped. The distillate was separated by light petroleum into brownish-red crystals of bromoselenobenzene (m. p. 61°) and very hygroscopic, colourless plates, m. p. 46° (see below). The undistilled residue was separated by means of warm light petroleum into bromoselenobenzene and diphenyl diselenide (m. p. 63°). (*b*) Phenylselenoglycollic acid dibromide (3·7 g.) was melted and the cooled melt extracted several times with cold light petroleum; the residue consisted of almost colourless crystals which separated from hot light petroleum in transparent, colourless leaflets, m. p. 46—47°, either alone or when mixed with bromoacetic acid. The extracts on evaporation gave bromoselenobenzene together with a small amount of diphenyl diselenide. It is therefore evident that phenylselenoglycollic acid dibromide decomposes at its m. p. mainly thus : $CH_2(SeBr_2Ph)\cdot CO_2H = PhSeBr + CH_2Br\cdot CO_2H$.

p-*Tolylmethylselenetine Bromide.*—A cold liquid mixture of *p*-tolylmethyl selenide (3·7 g.) and bromoacetic acid (2·8 g.), after standing over-night, set to a mass of long, glistening needles, which, when separated from the admixed oil by means of porous earthenware, weighed 3·7 g. A portion (0·2 g.) of this *p*-tolylmethylselenetine bromide was placed in a test tube and plunged into boiling water; the compound slowly melted, without visible effervescence, but a strong odour of methyl bromide was developed. The resulting oil immediately set to a crystalline mass, m. p. 96—97°, either alone or when mixed with *p*-tolylselenoglycollic acid (Morgan and Porritt, *loc. cit.*). 0·1964 G., heated until completely molten, lost 0·0582 g. (Found : loss, 29·7. Calc. for CH_3Br, 29·3%).

p-Tolylselenoglycollic acid dibromide (compare Morgan and Porritt, *loc. cit.*) was prepared by two methods. (*a*) A solution of bromine (1·4 g.) in carbon tetrachloride (25 c.c.) was added to a hot solution of *p*-tolylselenoglycollic acid (1·8 g.) in the same solvent (100 c.c.); the yellow needles of the additive compound (3·1 g.) melted at 103—104° to a deep red liquid. (*b*) A solution of bromine (0·4 g.) in carbon tetrachloride (25 c.c.) was added to a cold solution of *p*-tolylmethylselenetine bromide (0·65 g.) in carbon tetrachloride (300 c.c.); the yellow needles (0·8 g.), which began to separate immediately, had m. p. 100—101°, either alone or when mixed with the dibromide prepared as in (*a*).

Action of heat on p-*tolylselenoglycollic acid dibromide.* This compound (1·5 g.) was heated at its m. p. for a few minutes, and the deep red liquid, which set to a semicrystalline mass on cooling, was extracted several times with small amounts of cold light petroleum; the insoluble residue (0·43 g.) consisted of colourless, hygroscopic leaflets, m. p. 48—49° either alone or when mixed with bromoacetic acid. The extracts, on evaporation at the ordinary temperature, gave a reddish-brown oil which could not be induced to crystallise; that it is *p*-bromoselenotoluene is rendered highly probable by its ready reduction with aluminium amalgam in moist ethereal solution to di-*p*-tolyl diselenide, m. p. 47°; aluminium bromide was obtained on washing the ethereal solution with water.

p-*Bromoselenotoluene dibromide* was prepared by three methods. (*a*) *p*-Tolueneseleninic acid (1·02 g.) was triturated with concentrated aqueous hydrobromic acid (6 c.c.), and the orange-red powder (2 g., m. p. 80—90°) which separated was recrystallised from chloroform; red needles, m. p. 113—114° (decomp.). (*b*) A solution of bromine (0·5 g., 3 mols.) in carbon tetrachloride (15 c.c.) was added to a warm solution of di-*p*-tolyl diselenide (0·34 g.) in warm carbon tetrachloride (25 c.c.); on cooling, orange-red leaflets

(0·6 g.) separated, m. p. 114—115° (decomp.). (*c*) Solutions of bromine (0·9 g., 2 mols.) and of *p*-tolylselenoglycollic acid (0·57 g.) in chloroform (20 c.c. in all) were mixed and became warm; on cooling, deep red needles were deposited, m. p. 113—114° (decomp.) either alone or when mixed with the compound prepared as described under (*a*) or (*b*). There can be no doubt therefore that this compound is actually *p*-bromoselenotoluene dibromide, and not *p*-tolylselenoglycollic acid tetrabromide as supposed by Morgan and Porritt (*loc. cit.*). *p*-Bromoselenotoluene dibromide dissolves in hot water and the resulting colourless solution on cooling deposits colourless needles, m. p. 169—170° either alone or when mixed with *p*-tolylseleninic acid.

If preparation (*c*) be attempted in carbon tetrachloride, of which 100 c.c. are necessary to dissolve the acid, the sole product of the reaction is *p*-tolylselenoglycollic acid dibromide.

Phenyl methyl selenide dibromide was prepared by the addition of bromine (33 g.) in carbon disulphide (30 c.c.) to phenyl methyl selenide (35 g.) in the same solvent (120 c.c.). The warm solution deposited the additive compound almost immediately as long, yellow, glistening needles (yield 95%) which turned brown at about 100° and melted at 115—116° (decomp.); it is soluble in water to the extent of about 6%, and the colourless solution is acid to Congo-red and when cooled or concentrated deposits the dibromide unchanged in m. p. (Found : Br, 48·0. $C_7H_8SeBr_2$ requires Br, 48·3%).

Action of heat on phenyl methyl selenide dibromide. The dibromide (1·9940 g.) was heated at 120—130° for about 10 minutes, by which time decomposition had ceased. The evolved gas was passed into an alcoholic solution of silver nitrate and caused the precipitation of silver bromide. The loss in weight was 0·5684 g. or 28·50% (Calc. for loss of CH_3Br, 28·46%). The non-volatile residue set to a brownish-red, crystalline mass, m. p. 60—61°, which separated from light petroleum as deep garnet-red cubes, m. p. 61°, alone or when mixed with bromoselenobenzene.

Phenyl methyl selenide di-iodide was prepared by triturating the dibromide (2 g.) at 40° with a solution of potassium iodide (2 g.; 2 mols.) in water (10 c.c.). The chocolate-coloured powder obtained (2·65 g.; calc., 2·60 g.), after washing and drying had m. p. 67—70°, and crystallised from alcohol in glistening, purple, short prisms, m. p. 69—71° (Found : I, 59·4. $C_7H_8I_2Se$ requires I, 59·8%).

Phenyl methyl selenide bromo-iodide was prepared by triturating phenyl methyl selenide dibromide (3 g.) with a cold solution of potassium iodide (3 g.; 2 mols.) in water (15 c.c.). The bromo-iodide (3·5 g.) was deep red and separated from alcohol in red, ill-defined, compact crystals (3·1 g.), m. p. 85° (decomp.) (Found: Br + I, 55·5. C_7H_8BrISe requires Br + I, 54·8%). When triturated with a warm solution of potassium iodide it was immediately converted into the di-iodide, m. p. and mixed m. p. 67—70° (decomp.).

The action of heat on phenyl methyl selenide bromo-iodide. 1·0056 G. of the bromo-iodide were heated at 100° and the distillate was collected. The non-volatile residue weighed 0·7636 g. (Found: loss, 34·1. Calc., for MeI, 37·5%; for MeBr, 25·1%), and when crystallised from light petroleum had m. p. 61°, either alone or mixed with bromoselenobenzene. The distillate was a colourless liquid which was non-volatile at the ordinary temperature, contained iodine, and combined with pyridine on warming. Phenyl methyl selenide bromo-iodide therefore decomposes on heating according to the equation SePhMeBrI = SePhBr + MeI.

Phenyl methyl selenide dihydroxide was prepared by the trituration of a mixture of phenyl methyl selenide dibromide (10 g.), silver oxide (12 g.), and water (100 c.c.) until the yellow colour of the dibromide had disappeared. The colourless filtered solution on evaporation and desiccation gave about 8 c.c. of a viscous oil which could not be induced to crystallise. This compound was not analysed since it could not be completely freed from moisture without decomposition, but its identity was established by its immediate conversion into phenyl methyl selenide dibromide, m. p. 115—116°, on the addition of aqueous hydrobromic acid.

Action of heat on phenyl methyl selenide dihydroxide. The above compound (4 c.c.), contained in a small distilling flask, was gradually heated in an oil-bath; at 135—155° (bath temp.) some of the admixed water distilled, and at 175—180° one or two drops of an oily material distilled over and dissolved in the water into which the side-arm of the flask dipped; at 185°, a sudden decomposition ensued and some material distilled. The residue in the flask (about 1 g.) set immediately to a yellow, crystalline mass, m. p. 63—64°, after inoculation with a crystal of diphenyl diselenide. The water into which the products of decomposition had been led contained globules of oil, which was isolated with ether and distilled; the distillate (about 1 g.) had b. p. 202—203° and was identified as phenyl methyl selenide by its complete conversion into the dibromide, m. p. 115—116°. The water, after removal of the oil, gave a silver mirror with ammoniacal silver oxide, restored the colour to Schiff's reagent, gave the characteristic odour of formalin on evaporation, and left a small amount of white, amorphous, insoluble material. There can thus be little doubt that formaldehyde is one of the decomposition products of phenyl methyl selenide dihydroxide. Similar products were obtained when the decomposition was carried out at 100°/15 mm.

Phenyl ethyl selenide dibromide was prepared by mixing phenyl ethyl selenide (5·55 g.) and a solution of bromine (4·9 g.) in carbon disulphide (20 c.c.). After several hours, the separated crystalline material (10 g.), m. p. 79°, was crystallised from ether and obtained as light red, transparent, stout, prismatic rods melting at 84° to a deep red liquid (Found : Br, 46·4. $C_8H_{10}Br_2Se$ requires Br, 46·4%).

Action of heat on phenyl ethyl selenide dibromide. This compound (2·0044 g.) was heated in a bath at a temperature not exceeding 130° until decomposition was complete (10 mins.). The residue (1·3738 g.) set to a brownish-red, crystalline mass, m. p. 60—61°. The vapour evolved during the decomposition gave a copious precipitate of silver bromide when passed into an aqueous-alcoholic solution of silver nitrate. The decomposition of the dibromide therefore takes place according to the equation $SePhEtBr_2 = SePhBr + EtBr$ (Found : loss, 31·3. Calc. for loss of C_2H_5Br, 31·6%). The solid product of the decomposition separated from light petroleum as deed garnet-red cubes, m. p. 61° either alone or when mixed with bromoselenobenzene.

Interaction of Phenyl Ethyl Selenide and Bromoacetic Acid.—Phenyl ethyl selenide (5·55 g.) and bromoacetic acid (4·17 g.) were mixed and a little dry ether was added to render the mixture homogeneous. After standing for 3 weeks, the product had set to a mass of crystals, which, after draining on porous earthenware, had m. p. 35—36° either alone or when mixed with phenylselenoglycollic acid of m. p. 36—37°.

Action of Heat on Diphenyl Selenide Dibromide.—Diphenyl selenide and diphenyl diselenide were prepared by the method of Krafft and Lyons (*Ber.*, 1894, **27**, 1761). Diphenyl selenide dibromide was obtained in 95% yield by mixing bromine (4·9 g.) and diphenyl selenide (7 g.) each dissolved in 15 c.c. of carbon disulphide. This solvent is preferable to ether, since the m. p. of the diphenyl selenide dibromide (154°, unaltered by recrystallisation) obtained by its use is 14° higher than that recorded by Krafft and Lyons (*loc. cit.*). When heated, diphenyl selenide dibromide (5·0 g.) melted to a deep red liquid which effervesced vigorously owing to the evolution of hydrogen bromide. After 10 minutes, the evolution of gas ceased and the loss in weight was 20% (Calc. for 1HBr, 20·6%). The residue, a semi-solid mixture, was separated by means of light petroleum into an oil and an almost colourless, crystalline solid, which crystallised from hot light petroleum as glistening leaflets (0·5 g.), m. p. 115·5°. This compound is evidently dibromodiphenyl selenide, isolated by Krafft and Lyons (*loc. cit.*). The oil distilled completely at 196—198°/12 mm. to give an almost colourless liquid which deposited glassy crystals (2·0 g.), m. p. 32—33° (Found : Br, 25·6. $C_{12}H_9BrSe$ requires Br, 25·6%). Since this *compound* was the principal product of the thermal decomposition of diphenyl selenide dibromide, it follows that the main course of the reaction can be represented by the equation $SePh_2Br_2 = Ph{\cdot}Se{\cdot}C_6H_4Br + HBr$, and that the equation given by Krafft and Lyons, *viz.*, $2SePh_2Br_2 = Ph_2Se + (C_6H_4Br)_2Se + 2HBr$, represents a side reaction. These results explain why the attempt made by these authors to isolate diphenyl diselenide from the products of decomposition was unsuccessful.

Diphenyl selenoxide, prepared by the action of sodium hydroxide solution on diphenyl selenide dibromide, after recrystallisation from benzene had m. p. 113—114° (Krafft and Lyons, *loc. cit.*). This compound is more conveniently prepared by the following method : To diphenyl selenide (7 g.), perhydrol (10 c.c.) was added in small portions. The reaction mixture set, on cooling, to a crystalline mass; cold water was added and the product filtered, but as the selenoxide obtained weighed only 6·45 g. (instead of the calculated 7·5 g.), the aqueous filtrate (50 c.c.) was mixed with hydrobromic acid until no further reddish-yellow crystalline precipitate was formed. The latter, filtered and dried (1·75 g.), had m. p. 152—153° either alone or when mixed with diphenyl selenide dibromide. This result shows that diphenyl selenoxide is soluble in cold water to the extent of 2·2%. Diphenyl selenoxide, after crystallisation from benzene, has m. p. 113—114°, either alone or when mixed with the selenoxide prepared by the action of sodium hydroxide on diphenyl selenide dibromide.

The authors desire to express their indebtedness to the Government Grant Committee of the Royal Society for a grant which has helped to defray the cost of these investigations. One of them (W. R. G.) wishes to thank the Department of Scientific and Industrial Research for a maintenance grant which has enabled him to participate in this work.

BATTERSEA POLYTECHNIC, S.W. 11. [*Received, June* 18*th*, 1928.]