150. *The Products of the Interaction of Hydrogen Selenide and Ketones.*

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The interaction of hydrogen selenide and various ketones is shown to be accompanied by a reduction, involving hydrogen selenide, with the production of diselenides and not, as hitherto reported, dimeric seleno-ketones.

FOR some years it has been assumed that dimeric selenoketones may be prepared according to the equation

$$2RR'CO + 2H_2Se \longrightarrow (RR'C \cdot Se)_2 + 2H_2O$$

by treating a mixture of a ketone and concentrated hydrochloric acid with hydrogen selenide.[1]

Our interest in this class of reaction was stimulated by some observations made in the attempted preparation of selenobenzophenone by a modification of this method, carried out in absence of oxygen, a precaution which appears to have been previously neglected. Selenium was deposited and the product, odourless crystals (A), which gave analyses and molecular-weight values consistent with the formula $[(C_6H_5)_2CSe]_2$, decomposed smoothly at 200° to selenium and 1 : 1 : 2 : 2-tetraphenylethane in almost quantitative yield. Now the expected product of the pyrolysis of selenobenzophenone is tetraphenylethylene.[2] It was therefore concluded that (A) was, not dimeric selenobenzophenone, but bisdiphenyl-methyl diselenide, arising from a reduction in which hydrogen selenide was the active agent. This was confirmed by preparation of the diselenide by an unambiguous route.

The status of the compounds hitherto classed as dimeric selenoketones was thus compromised so we re-investigated them. Only three compounds described as diseleno-ketones seem to have been reported, all by Lyons and Bradt,[1] but the evidence given to support this classification is tenuous. The reactions claimed were re-examined, and the compounds obtained from the interaction of acetophenone, acetone, and ethyl methyl ketone with hydrogen selenide in the presence of hydrochloric acid, along with results of their pyrolysis are given in Table 1. No real comparison can be made between the compounds

TABLE 1.

Ketone	Product	Pyrolysis products
Acetophenone	Pleasant-smelling, yellow crystals (B), m. p. 54—56°	Se, PhEt, ? st́yrene polymer
Acetone	Amber, stinking oil (C), b. p. 64—66°/4·5 mm.	Se, 1 : 1 C_3H_8–C_3H_6
Ethyl methyl ketone	Golden, stinking oil (D), b. p. 92—93°/4·5 mm.	Se, 1 : 1 C_4H_{10}–C_4H_8

listed and those obtained by Lyons and Bradt owing to the paucity of information given by them.

In three cases elementary selenium, equal to half that contained in the total yield of the product, was recovered. The reaction with acetophenone gave less, probably owing to difficulty of separation of the products.

[1] Lyons and Bradt, *Ber.*, 1927, **60**, 824; Sidgwick, " The Chemical Elements and Their Compounds," Oxford, 1950.
[2] Kuhn, *J.*, 1938, 605.

The earlier workers do not mention the formation of selenium in their preparation of the alleged selenoketones, possibly because it was masked by adventitious production of the element by aerial oxidation of hydrogen selenide. By working in absence of oxygen we have shown the reaction to be :

$$2RR'CO + 3H_2Se = (RR'HC \cdot Se)_2 + 2H_2O + Se$$

This might be compared with a similar preparative reaction involving formaldehyde; [3] no selenium was deposited during treatment with hydrogen selenide [4] and the product was cyclic trimethylene triselenide. It is suggested that the initial step is the same for both aldehydes and ketones, namely, the formation of hydroselenohydrins :

$$RR'CO + H_2Se = HO \cdot CRR' \cdot SeH$$
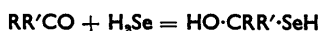
Indeed, such an addition compound of formaldehyde has been isolated [4] as a colourless heavy oil which slowly polymerises, liberating water. The fate of the hydroselenohydrin is, however, different in the two cases. With simple aldehydes, three molecules condense, in the presence of hydrochloric acid, to give a cyclic triselenide. With ketones it seems possible that water is eliminated from one molecule, giving the monomeric selenoketone, which, by analogy with certain thioketones, *e.g.*, thiobenzophenone, could exist as a fairly stable biradical. Such active entities would then be capable of attack on hydrogen selenide, undergoing reduction followed by dimerisation :

$$2RR'CSe + H_2Se = (RR'HC \cdot Se)_2 + Se$$
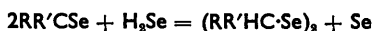
The traces of blue substance obtained on distillation of crude product (C) give support to the suggestion that monomeric selenoketones participate in some step of the reaction, as also does the observation that, in the early stages of the treatment of ketones with hydrogen selenide, the reaction mixtures become green and that this colour persists for some time before changing to the orange or red due to precipitation of selenium. Such phenomena have never been observed in this laboratory in parallel reactions with aldehydes.

TABLE 2.

Substance	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$	Substance	$\lambda_{max.}$ (mμ)	$\varepsilon_{max.}$
Compound (C)	305	500	Di-*sec.*-butyl diselenide	305	439
Di*iso*propyl diselenide	305	511	Bischloromethyl diselenide	305	380
Compound (D)	305	438	Selenium monochloride	305	3300

Analyses and molecular-weight determinations on all four compounds gave results compatible with either of the formulations $(RR'C \cdot Se)_2$ or $(RR'HC \cdot Se)_2$ but substances (A) and (B) were definitely identified as bisdiphenylmethyl diselenide and di-(1-phenylethyl) diselenide, respectively, by m. p.s and mixed m. p.s with authentic samples prepared by oxidation of the appropriate selenols. Substances (C) and (D) were identified as di*iso*propyl diselenide and di-*sec.*-butyl diselenide by means of the mercury compounds $(RR'HC \cdot Se)_2Hg$. Supporting evidence is the ultraviolet absorptions recorded in Table 2, where data for bischloromethyl diselenide and selenium monochloride are included for comparison.

Treatment of these compounds with halogen gave, in all cases, good yields of the corresponding substituted methyl halides. Elementary selenium was the other product when bromine was used, while it was selenium tetrachloride with chlorine. This is in line with the results of pyrolyses, for in both sets of experiments the products arise from substituted methyl radicals and not from the substituted methylene radicals implicit in a ketonic structure.

Finally, the results of the mercuration experiments and the iodine monochloride tests might be considered together, for both are explicable in terms of a weakening of the C–Se

[3] Bradt and Valkenburgh, *Proc. Indiana Acad. Sci.*, 1929, **39**, 165; Vanino and Schinner, *J. prakt. Chem.*, 1915, **91**, 116.
[4] Bridger and Pittman, *J.*, 1950, 1371.

bonds in the C–Se–Se–C chain resulting from electron delocalisations rendered possible by progressive phenylation at the terminal carbon atoms. Evidence for such delocalisation is given by a comparison of the difference of the molar refractivities of di*iso*propyl diselenide and di-(1-phenylethyl) diselenide, on the one hand, and that between two compounds in which optical exaltation accompanying phenyl substitution is improbable, say, *n*-hexane and *n*-pentylbenzene,[5] on the other.

Compound	R	ΔR for Ph minus Me
Di-(1-phenylethyl) diselenide	93·29 (25°)	20·31
Di*iso*propyl diselenide	52·66 (25°)	
n-Pentylbenzene	49·76 (20°)	19·83
n-Hexane	29·93 (20°)	

The alkyl diselenides (*C*) and (*D*) readily form compounds of the type $(RR'HC \cdot Se)_2Hg$ in almost 100% yield on treatment with metallic mercury at room temperature. At 125°

Ultraviolet absorptions of (———) compound (D), (— — — —) bischloromethyl diselenide, and (— · — · —) compound (B).
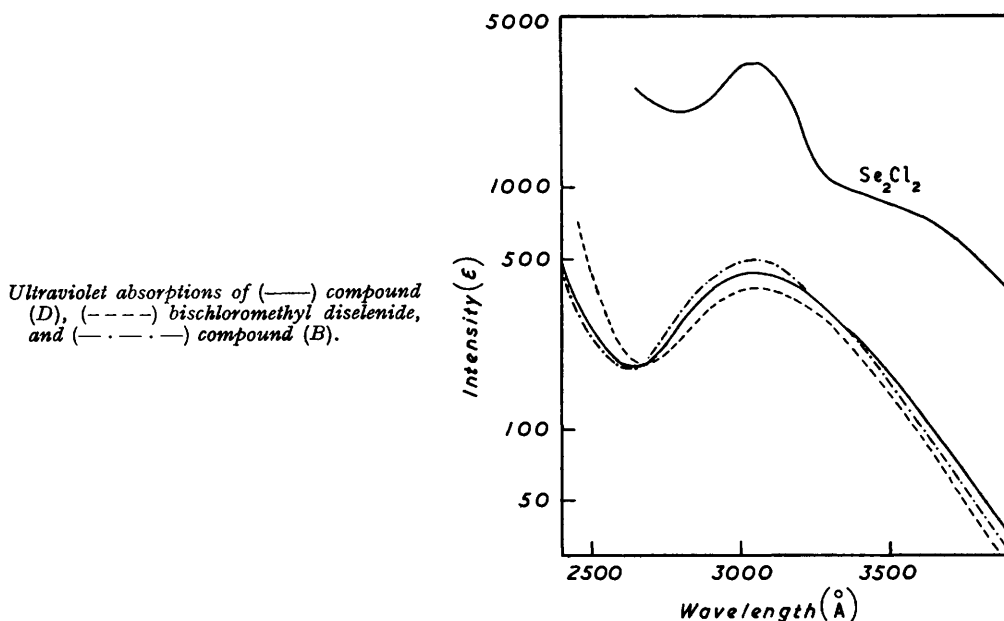
these compounds slowly decompose into the parent diselenide and mercury, only a small amount of mercury selenide being formed. No mercury compound is formed by the product (*A*) under these conditions; mercuric selenide is the only isolable product. In solution, the compound (*B*) gives an addition compound with mercury, which unlike those from (*C*) and (*D*) slowly decomposes in daylight with the production of mercuric selenide. At 125° it decomposes rapidly and completely, 99% of the mercury being recovered as mercuric selenide.

The liberation of 3 equiv. of iodine per atom of selenium on treatment of substances (*C*) and (*D*) with iodine monochloride corresponds to the formation of relatively stable alkylselenium trichlorides, compounds in which the C–Se bond remains inviolate. However, even at 0°, substances (*A*) and (*B*) react smoothly with iodine monochloride until some five atoms of iodine per atom of selenium are liberated. This corresponds to the formation of substituted methyl chlorides and selenium tetrachloride and gives no indication of the intermediate formation of compounds containing the C–Se bond.

[5] Partington, " An Advanced Treatise on Physical Chemistry," Vol. IV, Longmans, London, 1953.

EXPERIMENTAL

Interaction of Ketones and Hydrogen Selenide.—Essentially the same procedure was used in all cases. Hydrogen selenide was passed over the surface of a well-stirred mixture of the ketone and either concentrated hydrochloric acid or ethanolic hydrogen chloride. Either type of mixture gives the same products : that with ethanol absorbs hydrogen selenide more rapidly but gives a less pure product. Absence of oxygen was ensured by passing nitrogen through the reaction train at the beginning and end of the experiments.

Benzophenone. Benzophenone (20 g., 0·11 mol.) in ethanol (100 ml.) was treated with hydrogen chloride (0·4 mol.) followed by hydrogen selenide (0·67 mol.) introduced during 14 hr. Pale yellow crystals admixed with selenium separated and were filtered off. Leaching with hot ethanol gave 8·7 g. [0·018 mol. of $(C_{13}H_{11}Se)_2$; 32%] of yellow needles (A) and 1·63 g. (0·02 g.-atom) of selenium. Substance (A) recrystallised from light petroleum as odourless, pale yellow, felted needles, m. p. and mixed m. p. with *bisdiphenylmethyl diselenide*, 120—123° [Found : C, 62·3; H, 4·6; Se, 31·5%; M, cryoscopic in *cyclo*hexane, 464 ($\pm$5%). $C_{26}H_{22}Se_2$ requires C, 63·4; H, 4·5; Se, 32·1%; M, 492].

Acetophenone. Acetophenone (120 g., 1 mol.) in an ethanol (200 ml.) solution of hydrogen chloride (2 mol.), when treated with hydrogen selenide (2 mol.) during 8 hr., gave a pasty mixture of a heavy oil with red selenium, and a yellow supernatant liquid. The latter was mainly an ethanolic solution of hydrogen chloride and unchanged acetophenone and was rejected. The paste, on treatment with benzene (100 ml.) and filtration, gave 24 g. (0·3 g.-atom) of selenium. A clear red viscous oil (160 g.) [Found : Se, 44·7. Calc. for $(C_8H_9Se)_2$: Se, 42·9%] was obtained on removal of the benzene at 60°. This oil, the selenoacetophenone of Lyons and Bradt, is a mixture; its properties are not reproducible. Purification presented difficulties, as the substance could not be crystallised and normal distillation under reduced pressure caused decomposition. On short-path distillation at <1 mμ the red oil (11·8 g.) yielded six fractions by stepwise increase of the still temperature from 45° to 65°, leaving an involatile residue (1·67 g.). The first fraction (2·47 g., n_{α}^{20} 1·5870) contained about 40% of acetophenone. The remainder (6·675 g.; n_{α}^{20} 1·6464—1·6659), which deposited crystals, were bulked, dissolved in 3 : 1 methanol–ether (35 ml.), and cooled to −80°. Yellow prisms, with a pleasant odour resembling that of acetophenone (compound B) (3·29 g.) were obtained, having m. p. and mixed m. p. with *di-(1-phenylethyl) diselenide*, 54—56°, n_{α}^{60} 1·6352, d^{60} 1·407 [Found : Se, 42·7%; M, cryoscopic in *cyclo*hexane, 355 ($\pm$5%). $C_{16}H_{18}Se_2$ requires Se, 42·9%; M, 368].

Acetone. Hydrogen selenide (2 mol.) was passed over acetone (58 g., 1 mol.) in an equal volume of concentrated hydrochloric acid, during 9 hr. The dark oily layer which separated was removed, diluted with an equal volume of carbon tetrachloride, and filtered, the elementary selenium recovered being reserved. The solvent was removed under nitrogen, and the residual oil (48·6 g.) distilled under a reduced pressure of nitrogen. The main fraction (39·1 g., 0·16 mol. of $C_6H_{14}Se_2$), compound (C), had b. p. 64—66°/4·5 mm., n_{α}^{26} 1·5486, d^{25} 1·473 (Found : Se, 64·5%; M, cryoscopic in *cyclo*hexane, 245. $C_6H_{14}Se_2$ requires Se, 64·7%; M, 244). The elementry selenium left in the still was washed with carbon tetrachloride, combined with that recovered earlier, dissolved in nitric acid, and reprecipitated (16·0 g., 0·2 g.-atom). It is noteworthy that three drops of the first runnings in the distillation of the crude product were bright blue, and that this colour faded and could not be regained.

Ethyl methyl ketone. The same procedure was used as in the preceding preparation; 72 g. (1 mol.) of ethyl methyl ketone gave 21·5 g. (0·27 g.-atom) of elementary selenium and 68 g. (0·25 mol. of $C_8H_{18}Se_2$) of compound (D), b. p. 92—94°/4·5 mm., n_{α}^{25} 1·5392, d^{25} 1·382 (Found : Se, 58·0%; M, cryoscopic in *cyclo*hexane, 271. $C_8H_{18}Se_2$ requires Se, 58·1%; M, 272).

Preparation of Diselenides.—The procedure used in all cases was essentially the same. The selenol was prepared by treatment of the appropriate substituted methyl bromide with sodium hydrogen selenide, made by saturating an ethanolic solution of sodium ethoxide with hydrogen selenide, in the absence of air. Only in one case was the selenol isolated; in the others, the diselenide was formed by direct oxidation of the sodium salt of the selenol with hydrogen peroxide.

Bisdiphenylmethyl diselenide. Diphenylmethyl bromide (120 g.) was treated with sodium hydrogen selenide from sodium (12 g.) in ethanol (400 ml.). Then water (500 ml.) and 10N-sodium hydroxide (100 ml.) were added, followed by M/8-hydrogen peroxide (200 ml.). The

diselenide separated as a pasty mass, yielding, after two recrystallisations from ethanol, pale yellow needles (20 g.), m. p. 120—123° (Found : Se, 32·1%).

Di-(1-phenylethyl) diselenide. 1-Phenylethyl bromide (176 g.) was treated with sodium hydrogen selenide from sodium (12 g.) and ethanol (200 ml.). After 15 minutes' refluxing, the selenol was precipitated by addition of water, separated, dissolved in 10N-sodium hydroxide solution (200 ml.), washed with light petroleum, and reprecipitated with acetic acid. The crude 1-*phenylethaneselenol* (80 g.) was distilled under reduced pressure of nitrogen, giving a yellow, foul-smelling oil, b. p. 87—89°/8 mm. (Found : Se, 41·8%; *M*, cryoscopic in *cyclo*-hexane, 180. $C_8H_{10}Se$ requires Se, 42·7%; *M*, 185).

1-Phenylethaneselenol (12·8 g.), dissolved in aqueous 4N-sodium hydroxide (30 ml.), was oxidised with M/3-hydrogen peroxide (30 ml.). A yellow oil separated; it was diluted with light petroleum, washed with water, and dried ($MgSO_4$), and the solvent pumped off. The product was partly crystalline at room temperature. The crystals were removed and a second crop was obtained by cooling a solution of the filtrate in 1 : 1 methanol–ether to −80°. The two crops were combined and recrystallised from the same solvent, giving di-(1-phenylethyl) diselenide (3·78 g.), m. p. 54—56° (Found : Se, 43·4%). The liquid fraction, obtained by removal of solvent from the mother-liquors, was purified by molecular distillation. The distillate, which definitely contained no selenol, very slowly deposited crystals (2·24 g.) identical with those obtained earlier.

Diisopropyl diselenide. *iso*Propyl bromide (100 g.) and sodium hydrogen selenide, from sodium (18·7 g.) and ethanol (500 ml.), were refluxed for 10 min. 10N-Sodium hydroxide (100 ml.) and 2M-hydrogen peroxide (250 ml.) were added with cooling, and the resulting diselenide precipitated as a dark red oil by addition of water (1·5 l.). This oil was separated and fractionated *in vacuo*, giving di*iso*propyl diselenide (28 g.), b. p. 66—67°/4·5 mm., n_α^{25} 1·5479, d^{25} 1·472 (Found : Se, 64·6%; *M*, cryoscopic in *cyclo*hexane, 246).

Di-sec.-butyl diselenide. The procedure was as for the *iso*propyl compound. *sec.*-Butyl bromide (92 g.) gave crude diselenide (78 g.) which on vacuum distillation yielded the diselenide as a golden, stinking oil, b. p. 90—92°/4·5 mm., n_α^{25} 1·5390, d^{25} 1·381 (Found : Se, 58·3%; *M*, cryoscopic in *cyclo*hexane, 268).

Pyrolysis of Selenium Compounds.—Benzophenone derivative. Substance (*A*) (0·85 g.) was heated at 200° for 20 min. in a Pyrex tube under water-pump vacuum. A crystalline, selenium-free sublimate (0·53 g.) formed in the cold end of the tube and a fused bead of selenium (0·27 g.) was left behind. The sublimate recrystallised from benzene as colourless needles, m. p. 209—210°, mixed m. p. with tetraphenylethane 208—209°, with tetraphenylethylene 190°.

Acetophenone derivative. Substance (*B*) (3·087 g.) was heated at 290—300° for 30 min. in a sealed Pyrex tube. The products were separated by vacuum-distillation into liquid-air traps, a fused bead of selenium (1·282 g.) and a very small amount of benzene-soluble tar matter being left in the still. Two fractions were obtained of widely differing volatility. The first (0·920 g.) was a mobile liquid, distillation range 133—135°, showing no unsaturation (Hanus method) which formed a sulphonamide, m. p. and mixed m. p. with that from ethylbenzene 110—112°. The second (0·313 g.) was a viscous liquid of very high b. p. (Found : *M*, cryoscopic in *cyclo*-hexane, 199; unsaturation equiv. to 0·724 mmole of an ethylene). This figure corresponds to one double bond per 2·2 moles if the cryoscopic value of *M* is accepted. Thus this fraction would appear to be a mixture of " distyrenes " (*M*, 212) including *ca.* 50% of " distyrene II " which is a saturated, presumably cyclic compound.[6]

Acetone derivative. Substance (*C*) (0·3445 g.) was heated at 290—300° for 30 min. in a sealed Pyrex tube. The products were a selenium bead (0·218 g.) and a mobile liquid. The tube was cooled to −80°, unsealed, and put in the cooled limb of an inverted U-shaped still which was then pumped out and sealed. The volatile products were trapped in the other limb by manipulation of the cooling bath, sealed off, and weighed (0·105 g.). The distillate was liquid at −179° and boiled between −36° and −20°. It was dissolved, with suitable precautions, in chloroform, and the unsaturation estimated (Hanus method). This was equivalent to 1·25 mmoles of an ethylene. The b. p.s of the hydrocarbons which might be expected to be formed are : propane −47° (m. p. −190°), propene −42° (m. p. −185°), 2 : 3-di-methylbutane 58° (m. p. −135°), 2 : 3-dimethylbutene 73°; 1·25 mmoles of propane + 1·25 mmole of propene = 0·108 g. The distillate can only be an equimolar mixture of propane and propene.

[6] Thorpe, " Dictionary of Applied Chemistry," Vol. IV, 4th Ed., Longmans, London, 1940.

Ethyl methyl ketone derivative. The pyrolysis and separation of the products were carried out as for the acetone derivative. Compound (*D*) (0·359 g.) gave 0·204 g. of selenium and 0·143 g. of distillate, b. p. 0—5°, unsaturation equiv. to 1·205 mmoles of an ethylene. 1·205 mmoles of butane + 1·205 mmoles of butene = 0·138 g. The b. p.s of the revelant hydrocarbons are : *n*-butane −0·5°, but-1-ene −5°, but-2-ene 1° and 2·5°, 3 : 4-dimethylhexane 116°, 3 : 4-dimethylhex-3-ene 113·5°.

Halogenation of Selenium Compounds.—Benzophenone derivative. Compound (*A*) (3·0 g.), in carbon tetrachloride (25 ml.), was treated with 2% w/v bromine in carbon tetrachloride (50 ml.), giving a brown solution which rapidly deposited selenium. This was filtered off, the solvent removed, and selenium-free diphenylmethyl bromide (2·34 g.), b. p. 178°/17 mm., recovered by vacuum-distillation. Recrystallised from ether at −80° it had m. p. and mixed m. p. 39—40° (Found : Br, 32·8. Calc. for $C_{13}H_{11}Br$: Br, 32·4%).

Acetophenone derivative. Compound (*B*) (3·42 g.), in carbon tetrachloride (50 ml.), was treated with excess of chlorine, giving a deep red solution which, after a few minutes, deposited selenium tetrachloride. This was filtered off, the solvent removed, and 1-phenylethyl chloride (1·72 g.), b. p. 72°/14 mm., was recovered by vacuum-distillation (Found : Cl, 26·4. Calc. for C_8H_9Cl : Cl, 25·3%). The high chlorine content is probably due to the presence of selenium tetrachloride; the substance contained a trace of selenium which could not be removed by a second vacuum-distillation. The chlorine compound was hydrolysed by prolonged treatment with water, and the resulting alcohol treated with phenyl *iso*cyanate, giving a phenylurethane, m. p. and mixed m. p. with that from 1-phenylethyl alcohol 89—90°.

Acetone derivative. Nitrogen was bubbled through bromine (3 g.) and then over compound (*C*) (4·5 g.). The dark product was distilled from a water-bath, giving *iso*propyl bromide (2·95 g.), b. p. 60°, and a residue of selenium. This compound gave an anilide (*via* the Grignard reagent and phenyl *iso*cyanate), m. p. and mixed m. p. 105—106°.

Ethyl methyl ketone derivative. Compound (*D*) (11·33 g.) in acetic acid (35 ml.) was treated at 100° with a solution (22 ml., 4·4N) of bromine in the same solvent. After 24 hr. the solution was decanted from selenium and diluted with water. A heavy lquid (9·2 g.) separated, which, on distillation, gave a selenium-free *sec.*-butyl bromide (4·6 g.), b. p. 91—92° (Found : Br, 57·6. Calc. for C_4H_9Br : Br, 58·3%).

Preparation of Mercury Compounds.—Acetophenone derivative. Compound (*B*) (0·806 g.), in light petroleum (5 ml.), was treated with mercury, in the dark, for 30 days at room temperature, crystals being removed from time to time. The total yield was 0·831 g., and the m. p. and mixed m. p. with *di*-(1-*phenylethylseleno*)*mercury*, 98—102° (decomp.) (Found : Se, 28·2; Hg, 35·5. $C_{16}H_{18}Se_2Hg$ requires Se, 27·8; Hg, 35·2%).

Acetone derivative. Compound (*C*) (0·83 g.) was treated with excess of mercury for 72 hr., giving crystals which were dissolved in chloroform and decanted. The solvent was pumped off at room temperature, and unchanged reactant removed by prolonged vacuum-treatment, leaving yellow crystals (1·03 g.), m. p. and mixed m. p. with *di*(*iso*propylseleno)*mercury*, 123—125°. Some decomposition takes place at the m. p. which is somewhat arbitrary; the figure given is that at which the sample as a whole becomes fluid and shows a meniscus (Found : Se, 34·5; Hg, 45·7%; *M*, cryoscopic in bromoform, 500 ± 10%. $C_6H_{14}Se_2Hg$ requires Se, 35·5; Hg, 45·1%; *M*, 445).

Ethyl methyl ketone derivative. The preparation was carried out as described for compound (*C*). Compound (*D*) (0·952 g.) gave yellow crystals (1·44 g.), m. p. 70—80°. Recrystallisation from 1 : 1 ethanol–chloroform at −80° raised the m. p. to 79—80°, mixed m. p. with *di*-(1-*methylpropylseleno*)*mercury*, 80—82° (Found : Se, 33·7; Hg, 43·2. $C_8H_{18}Se_2Hg$ requires Se, 33·4; Hg, 42·4%).

Pyroysis of Mercury Compounds.—The mercury compounds were heated in a short-path still at 120—125°/10 mm. until decomposition or distillation was complete.

The mercury compound from (*B*) was heated for 3 hr.; 0·334 g. (0·589 mmole) gave an involatile residue of mercuric selenide (0·1624 g., 0·581 mmole) and a distillate containing only a trace of elementary mercury.

The mercury compound from (*C*) was heated for 9½ hr.; 0·4556 g. (1·03 mmoles) gave a distillate containing a considerable proportion of undecomposed mercury compound and also 0·0617 g. (0·31 mg.-atom) of metallic mercury. An involatile residue of mercuric selenide (0·0185 g., 0·07 mmole) was left.

The pyrolysis of the mercury compound from (*D*) was essentially similar to that just

described. Much metallic mercury was observed on the cold finger and a mere trace of involatile residue remained. No weighings were made owing to the obnoxious nature of the material.

Iodine Monochloride Titrations.—The procedure described by McCullough, Campbell, and Krilanovitch [7] was modified by cooling the iodine monochloride solution to 0° and carrying out the addition of the sample and all subsequent operations at that temperature.

Benzophenone derivative. This gave indefinite end-points both at room temperature and at 0°, values of *ca.* 4·5—5·5 atoms of iodine per atom of selenium being obtained.

Acetophenone derivative. This gave an abnormal value of 5 ($\pm 2\%$) atoms of iodine per atom of selenium at room temperature and at 0°.

Acetone and ethyl methyl ketone derivatives. These gave very indefinite end-points at room temperature, but at 0° the usual figure of 3 ($\pm 1\%$) atoms of iodine per atom of selenium was obtained.

The authentic diselenides gave results identical with those above.

Analytical.—*Estimation of selenium.* Some difficulty was experienced in the destruction of the organic part of aromatic selenium compounds by wet methods. However, combustion in a Grote–Krekeler tube [8] with a rapid flow of wet air (*ca.* 2 l./min.) usually resulted in complete oxidation, although, in some cases, traces of red selenium were occasionally deposited. The use of air enriched with an equal volume of oxygen at a rate of flow of 700 ml./min. eliminated this. The selenium dioxide formed was estimated by titration with potassium permanganate.

Estimation of selenium and mercury together. With the mercury compounds, the sample was heated under reflux with 3—5 ml. oleum until thoroughly charred, and the oxidation completed by dropwise addition of 30% hydrogen peroxide until the mixture was clear. This solution was diluted with water (25 ml.), concentrated hydrochloric acid (100 ml.) added, and the selenium precipitated at room temperature by addition of saturated aqueous sulphur dioxide (15 ml.). The precipitate was washed three times with concentrated hydrochloric acid, once with cold water, and then converted into the black form by washing with hot water. The filtrate was nearly neutralised with ammonia, and the mercury precipitated as the sulphide with hydrogen sulphide. The admixed sulphur was removed by extraction with carbon disulphide.

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[7] McCullough, Campbell, and Krilanovitch, *Ind. Eng. Chem. Anal.*, 1946, **18**, 638.
[8] Grote and Krekeler, *Angew. Chem.*, 1933, **46**, 106.