401. *The Oxidation of Organoselenium Compounds by Ozone.*

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Dialkyl and diaryl monoselenides are oxidised to selenoxides by an equimolar quantity of ozone. Diselenides react with three mol. of ozone, to give seleninic anhydrides; the same products are formed on oxidation with t-butyl hydroperoxide under anhydrous conditions. In neither case were intermediate products isolable. A possible mechanism of oxidation is discussed and the rates of ozonisation of mono- and di-selenides are compared with those of olefins and sulphides. A method for the preparation of the hitherto unknown seleninyl chlorides Ar·SeOCl is presented.

THE reaction of an organic monoselenide with ozone has received only one mention in the literature,[1] compared with the several, reviewed by Bailey,[2] to the ozonisation of sulphur compounds. Reactions of organoselenium compounds with other oxidants have been more extensively examined; for instance, hydrogen peroxide yields selenoxides from

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[1] Smedslund, *Finska Kemistamf. Medd.*, 1932, **41**, 13.

[2] Bailey, *Chem. Rev.*, 1958, **58**, 925.

diaryl selenides [3] but seleninic acids from alkyl aryl and dialkyl selenides [4,5,6] and from diaryl diselenides.[7]

Solutions of dialkyl and diaryl mono- and di-selenides in carbon tetrachloride, nitromethane, or chloroform at temperatures ranging from −10° to −50° removed ozone completely from an accurately controlled stream of ozonised oxygen until a well-defined end-point was reached. Fig. 1 represents typical uptake curves. After the end-point no further reaction of ozone with the products was detected, except to a minor extent in the case of one dialkyl monoselenide.

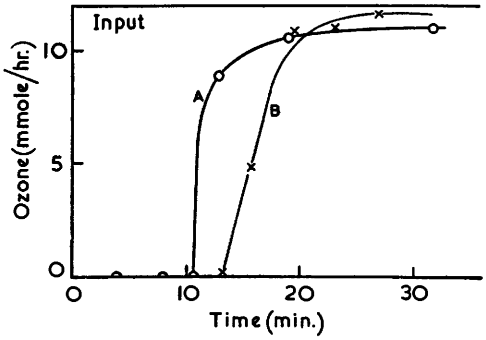

FIG. 1. Ozonisation of (A) diphenyl selenide ($2{\cdot}2 \times 10^{-3}$ mole) in nitromethane (10 ml.) and carbon tetrachloride (4 ml.) at −18°, and (B) diphenyl diselenide ($8{\cdot}1 \times 10^{-4}$ mole) in nitromethane (40 ml.) at −10°.

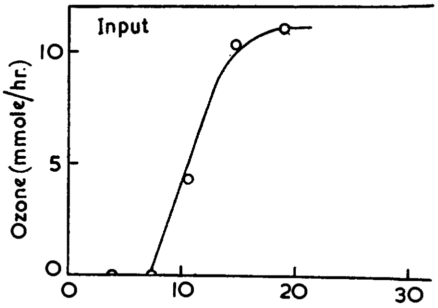

FIG. 2. Ozonisation of benzeneselenenyl chloride ($1{\cdot}4 \times 10^{-3}$ mole) in carbon tetrachloride (30 ml.) at −20°.

Products and Stoicheiometry.—(*a*) *Monoselenides.* After ozonisation to the exact end-point the removal of solvent below room temperature left in all cases a quantitative yield of selenoxide, contaminated only by traces of acidic impurities. The virtual absence of impurities and reagents facilitated further purification, by low-temperature recrystallisation, of even the more unstable dialkyl selenoxides, which are difficult to prepare by other methods.[6]

As indicated by the uptake curves, an excess of ozone did not yield selenones, which contrasts with the ready formation of sulphones from sulphoxides.[8] It is well known that oxidation to the sexivalent state is less readily achieved with selenium than with sulphur. Products of C–Se bond scission became evident on ozonisation of di-n-butyl selenoxide, which was particularly sensitive to decomposition generally.

The observed end-point always occurred accurately at an uptake of 1 mol. of ozone with a range of solvents, temperatures, and concentrations. This is unlike the variable stoicheiometry for monosulphides and phosphite triesters which has been explained by Thompson [9] on the basis of the formation of an initial complex of ozone with the oxidisable atom. If the exact stoicheiometry found here reflects the inability of selenium to form such an addition complex this may help to explain the divergence of reaction paths in the ozonisation of disulphides and diselenides discussed below.

(*b*) *Diselenides.* The end-point for the reaction with diselenides occurred at an uptake of 3 mol. of ozone. The products, which contained oxygen equivalent to one atom per mole of ozone, were seleninic anhydrides (I). The so-called sulphinic anhydrides have

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[3] Edwards, Gaythwaite, Kenyon, and Phillips, *J.*, 1928, 2293.
[4] Chierici and Passerini, *Boll. sci. Fac. Chim. ind. Bologna*, 1953, **11**, 104.
[5] Woodbridge, M.Sc. Thesis, London, 1959.
[6] Bird and Challenger, *J.*, 1942, 570.
[7] McCullough and Gould, *J. Amer. Chem. Soc.*, 1949, **71**, 674.
[8] Böhme and Fischer, *Ber.*, 1942, **75**, 1310.
[9] Thompson, *J. Amer. Chem. Soc.*, 1961, **83**, 845.

recently been shown[10] to possess the structure of the sulphur analogue of (II), but the authentic anhydride nature of the present products is suggested by the following evidence.

$$\underset{\text{(I)}}{\mathrm{R{\cdot}SeO{\cdot}O{\cdot}SeO{\cdot}R}} \qquad \underset{\text{(II)}}{\mathrm{R{\cdot}SeO_2{\cdot}SeO{\cdot}R}} \qquad \underset{\text{(III)}}{\mathrm{R{\cdot}SeO{\cdot}Se{\cdot}R}}$$

(*a*) The materials react extraordinarily readily with water, absorbing 1 mol., to yield 2 mol. of the seleninic acid, $\mathrm{R{\cdot}SeO_2H}$, even on exposure to the air. This reaction may be quantitatively reversed in the case of benzeneseleninic acid by heating *in vacuo*. The " sulphinic anhydrides " are stable in water. (*b*) Reaction with anhydrous ethanol yields seleninic acid and ethyl seleninate, the latter also being very sensitive to hydrolysis. (*c*) The infrared spectra are more compatible with structure (I) than with (II), the only bands in the regions expected for oxygenated selenium groups being a strong doublet in the region 830—860 cm.$^{-1}$, which is near the usual absorption by a selenoxide[11] (*ca.* 820 cm.$^{-1}$), thought to be due to an in-phase and out-of-phase vibration of the two Se=O groups in (I). (*d*) The oxidation of a diselenide to a compound (II) would be expected to involve the difficult transformation of $>$SeO into $>\mathrm{SeO_2}$; the ozonisation curves show no evidence of such a step.

The ozonisation of diselenides provides a simple and direct route to seleninic anhydrides, only two examples of which have been previously reported,[12,13] and, after hydrolysis, seleninic acids. The latter can be readily obtained from diselenides by using other oxidants but often contain coloured impurities which are difficult to remove.[7] Moreover, seleninic acids are amphoteric and may yield salts with acidic oxidants such as nitric acid.[14]

Mechanism of Ozonisation.—The oxidation of monoselenides to selenoxides is considered to involve a simple donation of oxygen by ozone to a nucleophilic centre:

The formation of the oxygen bridge in the conversion of diselenides into seleninic anhydrides presents an intriguing problem. Disulphides have been shown to give somewhat similar products, sulphonic anhydrides, by a mechanism which postulates the incorporation of a molecule of ozone as the rate-determining step.[15] This explains the stoicheiometry observed in this case, 5 atoms of oxygen being supplied by 3 molecules of ozone. Clearly, with diselenides, 3 molecules of ozone each donate 1 atom of oxygen and there can be no incorporation of ozone as such.

Convincing evidence that ozone is merely acting as an oxidant is to be found in the quantitative oxidation of diselenides to seleninic anhydrides by t-butyl hydroperoxide (3 mol.) under anhydrous conditions. Thus the formation of the anhydride structure cannot be sought in the rearrangement of an initial ozone adduct as postulated for disulphides.

No intermediate products were detectable in the oxidation of diselenides with either ozone or t-butyl hydroperoxide; a fractional equivalence of oxidant resulted in the calculated quantities of anhydride and unchanged diselenide.

A recent study of the oxidation of disulphides by peroxy-compounds has shown that the disproportionation of the intermediate thiolsulphinates is a key reaction in the formation of thiolsulphonates.[16] Small amounts of acidic products are also formed in the disproportionation, almost certainly as anhydrides when water is absent. The rearrangement

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[10] Bredereck, Wagner, Beck, and Klein, *Chem. Ber.*, 1960, **93**, 2736.

[11] Barnard, Fabian, and Koch, *J.*, 1949, 2442.

[12] Doughty, *Amer. Chem. J.*, 1909, **41**, 326.

[13] Buehler, Harris, and Arendale, *J. Amer. Chem. Soc.*, 1950, **72**, 4953.

[14] Backer and van Dam, *Rec. Trav. chim.*, 1935, **54**, 531.

[15] Barnard, *J.*, 1957, 4547 and unpublished work.

[16] Barnard and Percy, *Chem. and Ind.*, 1960, 1332.

of a sulphinylsulphone to a sulphonic sulphenic anhydride has been recently proposed as part of the mechanism of decomposition of sulphinic acids:[17]

$$\mathrm{R{\cdot}SO{\cdot}SO_2{\cdot}R \longrightarrow R{\cdot}S{\cdot}O{\cdot}SO_2{\cdot}R}$$

It is very probable that selenolseleninates (III) would be the first products of oxidation of diselenides and that the decomposition of these unknown, and almost certainly unstable, compounds would lead to the observed anhydride structures. At least two modes of decomposition can be suggested. (*a*) Homolysis, to give a resonance-stabilised seleninyl radical and a selenenyl radical. Dimerisation would lead to diselenide, together with a selenenic seleninic anhydride (steps 2 and 3) or to a selenenic anhydride (step 4). An analogous scheme has been proposed to explain the disproportionation of thiolsulphinates,[18]

$$\mathrm{R{\cdot}SeO{\cdot}Se{\cdot}R \longrightarrow (R{\cdot}\overset{\bullet}{Se}{:}O \longleftrightarrow R{\cdot}\overset{\bullet\bullet}{Se}{\cdot}O{\cdot}) + R{\cdot}\overset{\bullet\bullet}{Se}{\cdot}} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\mathrm{2R{\cdot}Se{\cdot} \longrightarrow R{\cdot}Se{\cdot}Se{\cdot}R} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$\mathrm{R{\cdot}\overset{\bullet}{Se}{:}O + R{\cdot}\overset{\bullet\bullet}{Se}{\cdot}O{\cdot} \longrightarrow R{\cdot}SeO{\cdot}O{\cdot}Se{\cdot}R} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$\mathrm{R{\cdot}\overset{\bullet\bullet}{Se}{\cdot}O{\cdot} + R{\cdot}Se{\cdot} \longrightarrow R{\cdot}Se{\cdot}O{\cdot}Se{\cdot}R} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

where step 4 does not occur and step 3 takes place with oxygen transfer to give thiolsulphonate. The formation of selenolselenonate, $\mathrm{R{\cdot}SeO_2{\cdot}Se{\cdot}R}$, in a similar manner is unlikely because it would involve raising selenium to the sexivalent state. (*b*) The high polarity of the Se=O bond[11] could induce an internal ionic rearrangement to give a selenenic anhydride without the free existence of scission fragments. In either (*a*) or (*b*) the anhydrides produced would, in the presence of an oxidant, be converted into the oxidation-resistant selenenic anhydride.

The Oxidation of an Unsymmetrical Diselenide.—In an attempt to distinguish between mechanisms (*a*) and (*b*), the oxidation of 2,4-dinitrophenyl phenyl diselenide was investigated. The selenium atom farthest from the deactivating effect of the nitro-groups was expected to be initially oxidised. Homolysis of the resulting selenolseleninate would give 2,4-dinitrobenzeneselenenyl radicals and hence, in all probability, bis-(2,4-dinitrophenyl) diselenide which, owing to its insolubility and pronounced resistance to oxidation, should remain as a stable product, particularly in partial oxidations. In fact, complete oxidation gave only the mixed anhydride of 2,4-dinitrobenzene- and benzene-seleninic acid, and partial oxidation resulted in the same anhydride and unchanged starting material.

Thus, unless radical dimerisation in (*a*) is assumed to proceed solely by step 4, these results favour mechanism (*b*) and the complete oxidation of a diselenide may therefore be pictured as:

$$\mathrm{R{\cdot}Se{\cdot}Se{\cdot}R \xrightarrow{i} R{\cdot}SeO{\cdot}Se{\cdot}R \longrightarrow R{\cdot}Se{\cdot}O{\cdot}Se{\cdot}R \xrightarrow{iii} R{\cdot}SeO{\cdot}O{\cdot}Se{\cdot}R \xrightarrow{iv} R{\cdot}SeO{\cdot}O{\cdot}SeO{\cdot}R}$$

Rate of Ozonisation.—By a series of competitive ozonisations the list of relative rates given in Table 1 was drawn up. The rates of steps (ii)—(iv), must be considerably greater than that of step (i) in view of the failure to isolate intermediates. An alkyl selenenate (Ar·Se·OR) can be considered to be the best available model of a selenenic anhydride (Ar·Se·O·Se·Ar) with regard to the oxidisability of the selenium atom. It was found that the replacement of the alkyl substituent of an alkyl aryl monoselenide by an alkoxy-group, *i.e.*, to give the selenenate, enhanced the rate of ozonisation. This had

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[17] Kice and Bowers, Abs. 140th Meeting of Amer. Chem. Soc., Sept. 1961, 70Q.

[18] Barnard, *J.*, 1957, 4675.

TABLE 1.

Relative rates of ozonisation.

Compound	Rate	Compound	Rate	Compound	Rate
Ph·Se·Ph	1	Ph·Se·Bu^n	4·1	Bu^n·Se·O·Bu^n	45 *
Ph·Se·Se·Ph	1·7	Bu^n·Se·Bu^n	34	Bu^n·S·Bu^n	$\ll 1$
Bu^n·Se·Se·Bu^n	2·9	Ph·Se·O·Bu^n	5·4 *	2-Methylpent-2-ene	< 1

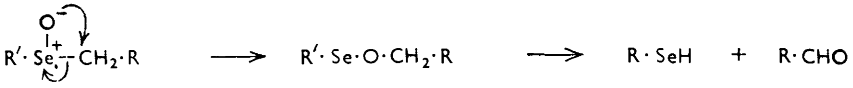
* Extrapolated from the rate of ozonisation of the appropriate monoselenide by using the factor 1·33 found to apply between the rates of ozonisation of ethyl 2,4-dinitrobenzeneselenenate and ethyl 2,4-dinitrophenyl selenide.

been noticed previously in the sulphur series, *e.g.*, methyl benzenesulphenate was ozonised more readily than methyl phenyl sulphide.[15] The rate of ozonisation of a selenenic anhydride might, therefore, be expected to compare with that of the parent diselenide at least as favourably as does the rate of an alkyl aryl or dialkyl monoselenide with a diaryl or dialkyl diselenide, respectively.

All the selenium compounds examined reacted more readily than olefins with ozone. As an extreme example, when di-n-butyl selenide competed with 2-methylpent-2-ene for an insufficiency of ozone all the olefin was recovered within the estimated experimental error of $\pm 2\%$. This contrasts with monosulphides which react with ozone at least 50 times more slowly than do olefins.[15]

The solid and odourless didodecyl monoselenide was tested for antiozonant activity in natural rubber vulcanizates. Although it was shown to react with ozone at least ten times as readily as antiozonants of the substituted *p*-phenylenediamine type, the selenide did little to protect rubber, suggesting that an ozone-scavenging mechanism is not important in this respect.

The Rearrangement of Selenolseleninates.—To confirm the postulated rearrangement of selenolseleninates, which closely resembles that previously suggested to explain the decomposition of dialkyl selenoxides: [19]



it was desirable to attempt the synthesis of these materials. Even if, as seems likely, they are too unstable to be isolated, their products of decomposition should be predictable.

Of the routes to their sulphur analogues, thiolsulphinates, the two most important are the oxidation of a disulphide [20] and the condensation of a thiol with a sulphinyl chloride.[21] The oxidation of a diselenide has just been described and was obviously not applicable here, while the condensation route required the synthesis of the hitherto unknown seleninyl chlorides. The reaction of seleninic acids with thionyl chloride,[5] and the controlled hydrolysis of arylselenium trichlorides failed to give the seleninyl chlorides which were finally prepared by the ozonisation of selenenyl chlorides:

$$\text{Ar·SeCl} + O_3 \longrightarrow \text{Ar·SeOCl} + O_2$$

Areneselenenyl chlorides reacted with exactly one mole of ozone in an anhydrous solvent at low temperatures (Fig. 2), giving high yields of the seleninyl chlorides. The latter were readily and quantitatively hydrolysed to seleninic acids and were converted by sodium alkoxides into the esters of seleninic acids.

Benzeneseleninyl chloride with benzeneselenol in the presence of pyridine, triethylamine, or anhydrous sodium carbonate gave products which, after contact with water, consisted of an equimolar mixture of diphenyl diselenide and benzeneseleninic acid. Under

[19] Campbell, Walker, and Coppinger, *Chem. Rev.*, 1952, **50**, 279.
[20] Small, Bailey, and Cavallito, *J. Amer. Chem. Soc.*, 1947, **69**, 1710.
[21] Backer and Kloosterziel, *Rec. Trav. chim.*, 1954, **73**, 129.

completely anhydrous conditions, an equivalent amount of benzeneseleninic anhydride replaced the seleninic acid. Since the anhydride could not be quantitatively separated from the reaction mixture it was estimated by ethanolysis under standard conditions and the determination of the ethanol liberated by subsequent hydrolysis of the seleninyl ester.

The stoicheiometry of the condensation may therefore be written:

$$3\mathrm{Ph{\cdot}SeH} + 3\mathrm{Ph{\cdot}SeOCl} \xrightarrow{\text{Base}} 2\mathrm{Ph{\cdot}Se{\cdot}Se{\cdot}Ph} + \mathrm{Ph{\cdot}SeO{\cdot}O{\cdot}SeO{\cdot}Ph}$$

Three suggestions can be made to explain the formation of a seleninic rather than a seleninic anhydride. (*a*) The selenenic anhydride disproportionates into the more stable selenenic anhydride and diselenide. It is difficult to see how such a disproportionation could occur without fragmentation of the molecule at some stage and this cannot be reconciled with the evidence obtained from the oxidation of the unsymmetrical diselenide. (*b*) Seleninyl chloride could oxidise the selenenic anhydride, in which case the overall reaction may be written:

$$\begin{gathered}\mathrm{Ph{\cdot}SeOCl} + \mathrm{Ph{\cdot}SeH} \longrightarrow [\mathrm{Ph{\cdot}SeO{\cdot}Se{\cdot}Ph}] \longrightarrow \mathrm{Ph{\cdot}Se{\cdot}O{\cdot}Se{\cdot}Ph}\\ 2\mathrm{Ph{\cdot}SeOCl} + \mathrm{Ph{\cdot}Se{\cdot}O{\cdot}Se{\cdot}Ph} \longrightarrow 2\mathrm{Ph{\cdot}SeCl} + \mathrm{Ph{\cdot}SeO{\cdot}O{\cdot}SeO{\cdot}Ph}\\ 2\mathrm{Ph{\cdot}SeCl} + 2\mathrm{Ph{\cdot}SeH} \longrightarrow 2\mathrm{Ph{\cdot}Se{\cdot}Se{\cdot}Ph} + 2\mathrm{HCl}.\end{gathered}$$

The formation during the reaction of a transient red-orange colour, typical of the selenenyl chloride, supports this hypothesis. In the absence of base, benzeneselenenyl chloride, and diphenyl diselenide, together with unchanged benzeneseleninyl chloride and water (or the hydrochloride of benzeneseleninic acid), were found. This shows that seleninyl chloride can act as an oxidant:

$$2\mathrm{Ph{\cdot}SeH} + 2\mathrm{Ph{\cdot}SeOCl} \longrightarrow \mathrm{Ph{\cdot}Se{\cdot}Se{\cdot}Ph} + \mathrm{Ph{\cdot}SeCl}\ (+\ \mathrm{Ph{\cdot}SeOCl} + \mathrm{H_2O})$$

Benzeneseleninyl chloride also reacted rapidly with selenides, but a simple oxygen transfer could not be established since the expected selenenyl chloride reacted further to give complex and intractable products. (*c*) Selenolseleninate might also oxidise selenenic anhydride and be itself reduced to diselenide:

$$2\mathrm{Ph{\cdot}SeO{\cdot}Se{\cdot}Ph} + \mathrm{Ph{\cdot}Se{\cdot}O{\cdot}Se{\cdot}Ph} \longrightarrow 2\mathrm{Ph{\cdot}Se{\cdot}Se{\cdot}Ph} + \mathrm{Ph{\cdot}SeO{\cdot}O{\cdot}SeO{\cdot}Ph}$$

in which case the overall process would simulate the disproportionation of selenolseleninate into diselenide and seleninic anhydride but would involve no fragmentation. If (*c*) were operative it would obviously replace steps (iii) and (iv) in the mechanism of the oxidation of a diselenide (p. 2092). This would then resemble the mechanism already suggested for the oxidation of a disulphide by peroxy-compounds in which the initially formed thiolsulphinate is regarded as disproportionating into the final product, thiolsulphonate, and disulphide.[16]

Whatever the detailed mechanism of decomposition of selenolseleninates may be, the fact that attempts to prepare them lead to the formation of seleninic anhydrides strongly suggests that they are involved, as transient intermediates, in the oxidation of diselenides.

EXPERIMENTAL

Solvents used were of " AnalaR " grade and were dried and fractionally distilled before use.

Organoselenium Compounds.—These were prepared by standard procedures and were fractionally distilled or recrystallised until analytically pure. Selenium in these compounds was determined by a standard micro-combustion technique, followed by iodometric estimation of the resulting selenious acid.[5] Their physical properties are described in Table 2.

Ozonisations.—The apparatus for the production, absorption, and estimation of ozone was essentially that described by Barnard.[15] It generated 12 mmoles of ozone per hr. with an oxygen flow of 8 l./hr.

Titrimetric Analysis of Products.—(i) Selenoxides (10—20 mg.) were dissolved in acetic acid

TABLE 2.

Compound	Ref.	M. p.	B. p./mm.	n_D^{20}	Found (%)			Required (%)		
					C	H	Se	C	H	Se
Selenides										
Me_2Se	6	—	57°/747	1·4890	—	—	—	—	—	—
Bu^n_2Se	—	—	82—83°/13	1·4753	50·0	9·4	—	49·75	9·4	—
$(Me\cdot[CH_2]_{10}\cdot CH_2)_2Se$	22	34·5—35°	—	—	69·4	12·6	19·4	69·1	12·1	18·9
Ph_2Se	23	—	85—86°/0·02	1·6488	—	—	34·0	—	—	33·9
$PhSeBu^n$	24	—	57°/0·001	1·5740	(Contained 18% of biphenyl)					
2,4-$(NO_2)_2C_6H_3\cdot SEt$	—	106—108	—	—	34·7	2·9	28·2	34·4	2·9	28·3
Diselenides										
$Bu_2^nSe_2$	25	—	62—63°/0·05	1·5408	—	—	—	—	—	—
$(Me\cdot[CH_2]_{10}\cdot CH_2)_2Se_2$	25	29—31	—	—	—	—	31·4	—	—	31·8
$(Ph\cdot CH_2)_2Se_2$	26	93	—	—	—	—	46·1	—	—	46·4
Ph_2Se_2	27	61—62	—	—	—	—	50·6	—	—	50·5
2,4-$(NO_2)_2C_6H_3\cdot Se_2Ph$	28	108·5—109·5	—	—	35·9	2·1	39·4	35·9	2·0	39·3
Other compounds										
$Ph\cdot SeCl$	29	61	—	—	38·2	2·7	42·3*	37·65	2·65	41·25*
2,4-$(NO_2)_2C_6H_3SeCl$	30	102·5—104	—	—	25·6	1·15	28·2	25·6	1·05	28·05
2,4-$(NO_2)_2C_8H_3Se\cdot OEt$	30	128—129	—	—	32·8	2·65	27·3	33·0	2·75	27·1
$Ph\cdot SeO_2H$	7	122—124	—	—	37·75	3·2	41·3	38·0	3·2	41·75
Ph_2SeO	3	112	—	—	—	—	30·9	—	—	31·7
$Ph\cdot SeH$	27	—	64·5—65°/13	1·6145	—	—	—	—	—	—

* Found: Cl, 18·2. Required: Cl, 18·5%.

(10 ml.), 1·5M-potassium iodide (10 ml.) was added, and the liberated iodine titrated with N/50-sodium thiosulphate. The oxidation equivalent, E_0, could then be calculated. (ii) Seleninic acids or anhydrides or seleninyl chlorides (20—30 mg.) were dissolved in out-gassed water (10 ml.) and titrated with N/50-sodium hydroxide to phenolphthalein, giving the neutralisation equivalent, E_N; acidification with 6N-sulphuric acid (30 ml.) and addition of 1·5M-potassium iodide (10 ml.) enabled E_0 to be determined as above.

Ozonisation of Monoselenides.—The following is a typical example. Di-n-butyl selenide (0·97 g.) in carbon tetrachloride (60 ml.) was ozonised at −10° to the reaction end-point which occurred sharply when 0·99 mol. of ozone had been absorbed. Removal of the solvent at reduced pressure left *di-n-butyl selenoxide* (1·05 g.), m. p. 53—55°. Recrystallisation from light petroleum–acetone at −30° gave the selenoxide as white, hygroscopic crystals, m. p. 55—56° (Found: Se, 37·4%; E_0, 103. $C_8H_{18}OSe$ requires Se, 37·8%; E_0, 104·5). The crude selenoxide contained some acidic material (46 mg. equiv. to 1·38 ml. of 0·02N-NaOH) and smelt of butyric acid. Partial ozonisation gave virtually theoretical yields of selenoxide; on over-ozonisation the selenoxide continued to take up ozone slowly to give oils containing larger amounts of acidic material.

Dimethyl selenoxide. Dimethyl selenide (1·0145 g.) in chloroform (50 ml.) at −50° had absorbed 1·00 mol. of ozone at the end-point and gave the selenoxide (1·204 g.), m. p. 83—85°, on removal of the solvent. After recrystallisation from light petroleum–acetone at −30° the m. p.[6] was 85—86° (Found: Se, 63·2%; E_0, 63. Calc. for C_2H_6OSe: Se, 63·2%; E_0, 62·5). A concentrated solution of the selenide (2·52 g.) in chloroform (10 ml.) at −30° was treated with ozone (0·00217 mole). After removal of solvent and excess of selenide *in vacuo*, the selenoxide (0·202 g., 75%), m. p. 85—86°, was isolated.

Didodecyl selenoxide. The selenide (1·007 g.) in carbon tetrachloride (60 ml.) at −10° was treated with 0·99 mol. of ozone, to give the selenoxide (1·03 g.), m. p. 87—88°, after

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[22] Denison and Condit, *Ind. Eng. Chem.*, 1949, **41**, 944.
[23] Schoeller, *Ber.*, 1919, **52**, 1517.
[24] Nardelli and Chierici, *Ann. Chim.* (*Italy*), 1952, **42**, 111.
[25] Stoner and Williams, *J. Amer. Chem. Soc.*, 1948, **70**, 1113.
[26] Houben-Weyl, " Methoden der Organischen Chemie," George Thieme, Stuttgart, 1955, 4th edn., Vol. IX, p. 1088.
[27] Foster, *Org. Synth.*, 1944, **24**, 89.
[28] Rheinboldt and Giesbrecht, *Chem. Ber.*, 1952, **85**, 357.
[29] Behaghel and Seibert, *Ber.*, 1933, **66**, 708.
[30] Lawson and Kharasch, *J. Org. Chem.*, 1959, **24**, 857.

recrystallisation, 89·5—90° [22] (Found: C, 66·0; H, 11·7; Se, 18·2%; E_0, 216·5. Calc. for $C_{24}H_{50}OSe$: C, 66·4; H, 11·6; Se, 18·2%; E_0, 216·8).

Diphenyl selenoxide. The selenide (0·1234 g.) in carbon tetrachloride (15 ml.) at −10° reacted with 1·00 mol. of ozone, to give the selenoxide (0·124 g.), m. p. 80—87°. After recrystallisation from light petroleum–benzene the m. p. and mixed m. p. with authentic selenoxide was 110—112° [3] (Found: Se, 31·4%; E_0, 124. Calc. for $C_{12}H_{10}OSe$: Se, 31·7%; E_0, 124·5).

Ozonisation of Diselenides.—Diphenyl diselenide was typical. At the well-defined end-point the diselenide (0·496 g.) in carbon tetrachloride (40 ml.) at −5° had absorbed 2·92 mol. of ozone. Removal of the solvent *in vacuo* left *benzeneseleninic anhydride* (0·57 g.), m. p. 118—120°. After recrystallisation from anhydrous benzene the m. p. was 124—126° (Found: Se, 43·3%; E_N, 182; E_0, 62. $C_{12}H_{10}O_3Se_2$ requires Se, 43·8%; E_N, 180; E_0, 60). The anhydride was also obtained, together with the theoretical amount of water, by heating benzeneseleninic acid at 140° for 1 hr. *in vacuo* or at 90° for 2 hr. and had m. p. 164—165° [12] which dropped to 124—126° on recrystallisation from benzene. The high-melting form was regenerated by crystallisation from a concentrated solution (seed) or by heating the other form *in vacuo*, when melting would occur only at 164°. Both forms depressed the m. p. of benzeneseleninic acid and very readily absorbed 1 mol. of water, to give the seleninic acid, m. p. and mixed m. p. 122—124°.[7]

Other diselenides under similar conditions absorbed almost exactly 3 mol. of ozone, to give high yields of the following anhydrides:

*Butane-*1*-seleninic anhydride*, m. p. 99—101° (Found: C, 30·0; H, 5·6; Se, 49·2%; E_N, 157; E_0, 51·5. $C_8H_{18}O_3Se_2$ requires C, 30·1; H, 5·7; Se, 49·3%; E_N, 160; E_0, 53·3). Hydrolysis gave butane-1-seleninic acid, m. p. 67—69° [14] (Found: Se, 46·1. Calc. for $C_4H_{10}O_2Se$: Se, 46·7%).

Dodecaneseleninic anhydride, m. p. 79—80° (Found: Se, 29·3%; E_N, 265; E_0, 87. $C_{24}H_{50}O_3Se_2$ requires Se, 29·0%; E_N, 272; E_0, 90·7), $\nu_{max.}$ (KBr disc) 857 and 863 cm.$^{-1}$.

Toluene-α-seleninic anhydride, m. p. (after low-temperature recrystallisation from light petroleum–chloroform), 104—104·5° (decomp.) (Found: Se, 40·4%; E_N, 190; E_0, 63. $C_{14}H_{14}O_3Se_2$ requires Se, 40·7%; E_N, 194; E_0, 64·7), $\nu_{max.}$ (KBr disc) 830 and 845 cm.$^{-1}$. *Toluene-α-seleninic acid*, m. p. 90—92° (decomp.) (Found: C, 41·3; H, 4·0; Se, 38·9. $C_7H_8O_2Se$ requires C, 41·4; H, 3·95; Se, 38·9%), was produced on exposure of the anhydride to the air.

Ozonisation of 2,4*-dinitrophenyl phenyl diselenide.* The diselenide (0·473 g.) in carbon tetrachloride (50 ml.) at −10° had reacted with 3·16 mol. of ozone at the end-point. Evaporation of the solvent left a pale yellow solid, m. p. 105—110° (decomp.), which was completely soluble in benzene and was identified as *benzeneseleninic* 2,4*-dinitrobenzeneseleninic anhydride*, m. p. 113—114° (decomp.) (from benzene) (Found: Se, 35·1%; E_N, 222; E_0, 77. $C_{12}H_8N_2O_7Se_2$ requires Se, 35·1%; E_N, 225; E_0, 75). Treatment of the diselenide (0·507 g.) with 1·5 mol. of ozone and removal of anhydride by extraction with sodium carbonate solution left a clear solution of unchanged diselenide (0·265 g.; total yield 104%), m. p. and mixed m. p. 106—109°, with no evidence of the insoluble bis-(2,4-dinitrophenyl) diselenide.

Partial ozonisation of other diselenides. Diphenyl diselenide was typical. The diselenide (0·498 g.) in carbon tetrachloride at −20° was treated with 1 mol. of ozone. The precipitated anhydride (0·153 g.), m. p. 120—122°, was filtered off and the filtrate evaporated, to give a yellow solid (0·359 g.) which contained acidic material (0·012 g. as anhydride; titration). Extraction of a solution of this residue in carbon tetrachloride with 2N-sodium hydroxide solution and removal of solvent left pure diphenyl diselenide (0·344 g.; total yield 104%), m. p. and mixed m. p. 61—62°.

Oxidation of Diselenides with t-Butyl Hydroperoxide.—A solution (*ca.* 0·7M) of diselenide in dry benzene was treated with three equivalents of t-butyl hydroperoxide at room temperature. The yellow colour of the diselenide was discharged and a white precipitate formed, the reaction being generally complete after 3—4 days. Removal of the solvent left a virtually quantitative yield of seleninic anhydride. Thus, typically, didodecyl diselenide (0·993 g., 0·002 mole) and t-butyl hydroperoxide (0·006 mole) in benzene (3 ml.) gave, after 3 days, dodecaneseleninic anhydride (1·012 g.) of m. p. 77—80°. After recrystallisation, the m. p. and mixed m. p. was 78—80° (Found: E_0, 90; E_N, 275). The rate of oxidation was increased by the presence of strong acid; 2,4-dinitrophenyl phenyl diselenide was oxidised to the mixed seleninic anhydride only in the presence of such an acid; the following illustrates also the use of an insufficiency of oxidant. The diselenide (0·381 g., 0·000947 mole), t-butyl hydroperoxide

(0·152 g., 0·00162 mole), and dodecanesulphonic acid (1 mole % calc. on the hydroperoxide) were dissolved in benzene (6 ml.). After 20 days at room temperature the mixed anhydride (0·0964 g.) of 2,4-dinitrobenzene- and benzene-seleninic acid was filtered off; after recrystallisation its m. p. and mixed m. p. was 113·5—115° (Found: C, 32·0; H, 2·4; Se, 35·1%; E_N, 224·5; E_0, 77. $C_{12}H_8N_2O_7Se_2$ requires C, 32·0; H, 1·8; Se, 35·1%; E_N, 225; E_0, 75). The solvent was removed from the filtrate and contained 8·6% of the original hydroperoxide. By the techniques previously described the residue was found to consist of the mixed anhydride (0·127 g.) and unchanged diselenide (0·173 g.; total 99%), m. p. and mixed m. p. 108—109°. Other diselenides, treated with less than the theoretical amount of oxidant, gave the calculated amounts of seleninic anhydride and unchanged starting material.

Seleninyl Chlorides.—Benzeneselenenyl chloride (3·0 g.) in carbon tetrachloride (60 ml.) was ozonised at $-10°$. The end-point occurred sharply at an ozone uptake of 1·00 mol. Removal of the solvent left a pale yellow solid (3·59 g.), m. p. 64—72·5°. Sublimation *in vacuo* gave pure *benzeneseleninyl chloride*, m. p. 75° (Found: C, 34·6; H, 2·75; Cl, 16·8%; E_N, 102·3; E_0, 69·5. C_6H_5ClOSe requires C, 34·7; H, 2·45; Cl, 17·1; E_N, 103·8; E_0, 69·2). The seleninyl chloride was hydrolysed rapidly in air to an oily hydrochloride of benzeneseleninic acid. After hydrolysis in water containing just sufficient sodium hydroxide to neutralise the hydrochloric acid, and evaporation to dryness, pure benzeneseleninic acid was extracted with benzene from the residue. Hydrolysis in dilute nitric acid and exact precipitation of chloride ion with silver nitrate left benzeneseleninic acid nitrate on evaporation to dryness *in vacuo*, m. p. (after recrystallisation from benzene) and mixed m. p. 109—112° (Found: E_N, 128; E_0, 84·5. Calc. for $C_6H_7NO_5Se$: E_N, 126; E_0, 84).

Similarly 2,4-*dinitrobenzeneseleninyl chloride* was prepared as a yellow solid melting indefinitely between 90° and 120° (decomp.) after recrystallisation at $-30°$ from chloroform–carbon tetrachloride (Found: C, 24·9; H, 1·5; Cl, 12·1%; E_N, 144; E_0, 103. $C_6H_3ClN_2O_5Se$ requires C, 24·2; H, 1·0; Cl, 11·9%; E_N, 149; E_0, 99·2). On hydrolysis this gave 2,4-dinitrobenzeneseleninic acid, m. p. 140—143° (decomp.) (Found: C, 26·5; H, 1·55%; E_N, 275; E_0, 102. Calc. for $C_6H_4N_2O_6Se$: C, 25·8; H, 1·45%; E_N, 279·2; E_0, 93).

Ozonisation of Ethyl 2,4-*Dinitrobenzeneselenenate.*—The ester (0·384 g.), in chloroform (40 ml.) at $-10°$ absorbed 1·15 mol. of ozone, to give yellow *ethyl* 2,4-*dinitrobenzeneseleninate* (0·406 g.), m. p. 65—70°. After recrystallisation from ethanol–light petroleum at low temperature the m. p. was 78—80° (Found: C, 32·2; H, 2·85%; E_N, 304·5; E_0, 108. $C_8H_8N_2O_6Se$ requires C, 31·3; H, 2·65%; E_N, 307·1; E_0, 102·4). The ester was readily hydrolysed to 2,4-dinitrobenzeneseleninic acid, m. p. 140—142°, and ethanol (detected by gas–liquid chromatography).

Ethyl Benzeneseleninate.—(*a*) Diphenyl diselenide (1·0 g.) in carbon tetrachloride (40 ml.) and ethanol (20 ml.) was treated with the theoretical amount of ozone at $-10°$. The oil (1·5 g.) left on removal of solvent was distilled in a short-path still at $45°/10^{-4}$ mm., to give *ethyl benzeneseleninate* (0·7 g.), m. p. 35—41° (Found: C, 44·3; H, 4·6%; E_N, 222; E_0, 76·7. $C_8H_{10}O_2Se$ requires C, 44·25; H, 4·65%; E_N, 217·1; E_0, 72·4), with benzeneseleninic acid as distillation residue. Reaction of ethanol with isolated benzeneseleninic anhydride gave the same ethyl ester (m. p. 42—44° after vacuum-sublimation) but in lower yield. This was made the basis of an analytical procedure to detect anhydride in the presence of seleninic acid. Ethanol (0·2361 g.) was distilled *in vacuo* on to benzeneseleninic anhydride (0·364 g.) and, after 1 hr. at room temperature, the excess of ethanol (0·2185 g.) was recovered by prolonged pumping *in vacuo*. The theoretical quantity of water (0·0189 g.) was distilled on to the residue and, after 1 hr., the ethanol released by hydrolysis was pumped off (0·0167 g.; n_D^{20} 1·3610; pure according to gas–liquid chromatography). The yield of ester was therefore 36·8% (ethanol reacted), 34·9% (ethanol released by hydrolysis), and was found to be reproducible ($\pm 2\%$) in many runs even when the anhydride was mixed with diphenyl diselenide, benzeneseleninic acid, etc.

(*b*) Benzeneselenenyl chloride (3·01 g.) was ozonised to the seleninyl chloride in ethanol (10 ml.) and treated with sodium ethoxide [sodium (0·4 g.) in ethanol (15 ml.)]. Sodium chloride was filtered off. The residue left on removal of solvent gave the ester on short-path distillation. Sublimation *in vacuo* gave colourless crystals, m. p. 42—44° (Found: C, 44·2; H, 4·6%; E_N, 208; E_0, 71·4).

The ester was hydrolysed readily in moist air and on treatment with the theoretical amount of water gave ethanol and benzeneseleninic acid in quantitative yield.

Condensation of Benzeneseleninyl Chloride with Benzeneselenol.—(*a*) *In presence of base.* Benzeneselenol (1·57 g.) and triethylamine (1·01 g.) in chloroform (10 ml.) were added during 30 min. to a stirred solution, held at −50°, of benzeneseleninyl chloride previously prepared *in situ* by ozonisation of the selenenyl chloride (1·915 g.) in chloroform (50 ml.). The mixture assumed a deep orange colour which faded towards the end of the reaction. The solvent was removed *in vacuo*, leaving an orange solid (4·58 g.), part (1·426 g.) of which was analysed for seleninic anhydride by ethanolysis as described above. The ethanol absorbed (0·0130 g.) and liberated on hydrolysis (0·0120 g.) indicated an anhydride content of 0·327 g. The oxidation equivalent of a second portion gave a maximum anhydride content of 26% by weight. The residue from the ethanolysis was divided between light petroleum (b. p. 30—40°) and water. Diphenyl diselenide (0·629 g.; m. p. 60—62°) was recovered from the petrol, and benzeneseleninic acid (0·274 g.; m. p. 121—123°) crystallised from the concentrated aqueous fraction. The total yields of diphenyl diselenide and benzeneseleninic anhydride, with, in parentheses, the theoretical yields based on the mechanism suggested on p. 2094, were therefore 2·02 g. (2·08 g.) and 0·88 g., by ethanolysis, 1·20 g. (1·20 g.), by titration, respectively.

Condensations in the presence of pyridine or anhydrous sodium carbonate gave similar results. After contact with water the products consisted of diphenyl diselenide and benzeneseleninic acid in equimolar amounts very close to those predicted by theory. Before hydrolysis benzeneseleninic anhydride was shown to be present but could not be quantitatively isolated. Fractional sublimation *in vacuo* separated the products cleanly but only under conditions which converted benzeneseleninic acid into anhydride.

(*b*) *Condensation in the absence of base.* Condensation of benzeneselenol (1·57 g.) and benzeneseleninyl chloride [from benzeneselenenyl chloride (1·915 g.)] was carried out as above but in the absence of base. A dark orange solution was obtained which left a black oil (3·402 g.) on evaporation. A sublimate of benzeneselenenyl chloride (1·117 g.), m. p. and mixed m. p. 60—62° [29] (Found: E_0, 185. Calc. for C_6H_5ClSe: E_0, 191·5), was obtained when this product was left in a high vacuum in contact with a receiver cooled in liquid nitrogen. The residue (2·273 g.) solidified and contained acid and oxidant, respectively equivalent to 31% and 32% of its weight of benzeneseleninyl chloride. Partition between light petroleum and water, as above, enabled diphenyl diselenide (1·47 g.) and benzeneseleninic acid (0·71 g.) to be isolated.

Oxidation of Benzeneselenol by t-Butyl Hydroperoxide.—Benzeneselenol (0·01 mole) in chloroform (0·8 g.) was treated *in vacuo* with t-butyl hydroperoxide (0·0025 mole). After 12 hr. the solvent and excess of benzeneselenol were distilled off in a high vacuum, leaving diphenyl diselenide (0·00246 mole), m. p. and mixed m. p. 61·5—62·5°. Water (0·0392 g.) was separated from the distillate.

Relative Rates of Reaction of Selenides, Sulphides, and Olefins with Ozone.—Competitive ozonisations were performed on equimolar mixtures of the above compounds chosen in pairs such that (*a*) suitable analytical methods were available so that the extent of reaction of each component could be determined and, (*b*) that all rates of ozonisation could be finally expressed relatively to that of diphenyl selenide. Where, as in the case of diselenides, more than one mol. of ozone was consumed, it was assumed that the primary attack of ozone is the rate-determining step. Hence in such combinations as

$$\mathrm{A} + \mathrm{O_3} \xrightarrow{k_1} \text{Intermediate} \xrightarrow[\text{Fast}]{\mathrm{O_3}} \text{Product}$$

$$\mathrm{B} + \mathrm{O_3} \xrightarrow{k_2} \text{Product}$$

the normal expression for relative rates of two second-order reactions was used,[31] *i.e.*, $r = k_1/k_2 = \log([A]/[A]_0)/\log([B]/[B]_0)$ where $[A]$ = concentration after time t, $[A]_0$ = original concentration, etc. Two examples illustrate the general methods. (1) Di-n-butyl selenide (0·447 g.) and 2-methylpent-2-ene (0·201 g.) in carbon tetrachloride (14 ml.) at −20° were treated with ozone (0·499 mol.). The solvent was distilled off *in vacuo* and found by infrared spectroscopy to contain all the original olefin. Gas–liquid chromatography of the distillate revealed no trace of acetone or propionaldehyde which are primary products of ozonolysis of 2-methylpent-2-ene. (2) Diphenyl selenide (0·00215 mole) and di-n-butyl diselenide (0·00215 mole) in

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[31] Friess and Weissberger, " Technique of Organic Chemistry," Interscience Publishers, Inc., New York, 1953, Vol. VIII, p. 108.

carbon tetrachloride (40 ml.) at $-10°$ were treated with ozone (0·001075 mole). The determination of butane-1-seleninic anhydride by titration indicated that $3{\cdot}13 \times 10^{-4}$ mole of diselenide (equiv. to $9{\cdot}39 \times 10^{-4}$ mole of ozone) and, by difference, $1{\cdot}36 \times 10^{-4}$ mole of monoselenide had been consumed. A correction was applied by the method of successive approximations for the small quantity of acid formed during the ozonisation of monoselenides.

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