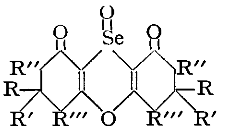
65. *Some New Organo-selenium Compounds.*

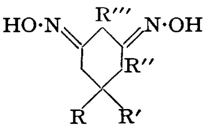
By F. E. King and D. G. I. Felton.

A new series of stable, red or orange organo-selenium compounds has been prepared by the oxidation of *cyclo*hexane-1 : 3-dione dioximes (II*a*—II*f*), using selenium dioxide. On the basis of analytical and physical data, these are called, tentatively, *7-nitroso-*$\Delta^{3:7}$*-dihydrobenz-*2 : 1 : 3-*oxaselenazoles* (III*a*—III*f*). Selenium dioxide does not oxidise 5-*phenyl*-2-*methyl*cyclo*hexane*-1 : 3-*dione dioxime* (II*g*). Five new octahydrophenoxaselenin-1 : 9-dione 10-oxides (I*a*, I*b*, I*d*, I*e*, I*g*) (cf. Stamm and Gossrau, *Ber.*, 1933, **66**, 1558; Borsche and Hartmann, *ibid.*, 1940, **73**, 839) have also been prepared.

It has been noted (Waitkins and Clark, *Chem. Reviews*, 1945, **36**, 235) that selenium dioxide oxidations often appear to proceed *via* the formation of unstable intermediate organo-selenium compounds and that normally they decompose largely into the oxidation product, selenium, and water. Cases are known, however, in which the greater proportion of the product consists of a stable organo-selenium compound and the above authors provide an exhaustive table of these cases. It is relevant to note, in particular, the reactions between aromatic *o*-diamines and selenium dioxide, whereby an interesting series of compounds known as the piaselenoles are obtained (Hinsberg, *Ber.*, 1889, **22**, 863, 866, 2897; 1890, **23**, 1393; 1891, **24**, 5. For a full list of references, see Waitkins and Clark, *loc. cit.*), and the analogous reaction between 4 : 5-diamino-2 : 6-dihydroxy-1 : 3-dimethylpyrimidine and selenium dioxide (Sachs and Meyerheim, *Ber.*, 1908, **41**, 3957) giving 2 : 6-dihydroxy-1 : 3-dimethylpiaselenopurine. The oxidation of 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione (" Dimedone ") by selenium dioxide, which yields the organo-selenium compound (I*c*) (Stamm and Gossrau, *loc. cit.*; Borsche and Hartmann, *loc. cit.*) is again a closely similar reaction.



(I*a*, R = R′ = R″ = R‴ = H; I*b*, R = Me, R′ = R″ = R‴ = H; I*c*, R = R′ = Me, R″ = R‴ = H; I*d*, R = Ph, R′ = R″ = R‴ = H; I*e*, R = R″ = Ph, R′ = R‴ = H; I*f*, R = R‴ = Ph, R′ = R″ = H; I*g*, R = R′ = Me, R″ = Ph, R‴ = H; I*h*, R = R′ = Me, R‴ = Ph, R″ = H.)



(II*a*, R = R′ = R″ = R‴ = H; II*b*, R = Me, R′ = R″ = R‴ = H; II*c*, R = R′ = Me, R″ = R‴ = H; II*d*, R = Ph, R′ = R″ = R‴ = H; II*e*, R = R″ = Ph, R′ = R‴ = H; II*f*, R = R′ = Me, R″ = Ph, R‴ = H; II*g*, R = Ph, R‴ = Me, R′ = R″ = H.)

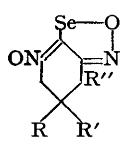
In the present work it was found that on attempted oxidation of *cyclo*hexane-1 : 3-dione dioxime (II*a*; Merling, *Annalen*, 1894, **278**, 28) by means of selenium dioxide, a very vigorous reaction occurred on heating the components in methanol or acetic anhydride, yielding in each case the same *product* as beautiful, long, red needles, containing selenium. Analysis indicated the empirical formula $C_6H_6O_2N_2Se$, and a micro-Rast molecular-weight determination confirmed this as the molecular formula. The reaction has been shown to be general for *cyclo*hexane-1 : 3-dione dioximes by the preparation of similar compounds starting from the following *cyclo*hexane-1 : 3-dione dioximes : 5-methyl (II*b*; Vorländer and Kalkow, *Ber.*, 1897, **30**, 1802), 5 : 5-dimethyl- (II*c*; Gittel, *Chem. Zentr.*, 1906 I, 34), 5-phenyl- (II*d*; Vorländer, *Ber.*, 1894, **27**, 2057), 4 : 5-*diphenyl*- (II*e*), and 4-*phenyl*-5 : 5-*dimethyl*- (II*f*). In all cases the products were highly crystalline red or orange-red compounds, the analyses of which agreed with the general formula $C_6H_3O_2N_2SeRR'R''$.

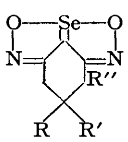
In sharp contrast, it was found that no such reaction occurred with a compound in which the 2-position in the dioxime was blocked; *e.g.*, 5-*phenyl*-2-*methyl*cyclo*hexane*-1 : 3-*dione dioxime* (II*g*) was recovered unchanged.

In general, the reaction appears to be stoicheiometrically: $C_6H_7O_2N_2RR'R'' + SeO_2 = C_6H_3O_2N_2SeRR'R'' + 2H_2O$, suggesting a dehydrogenation process coupled with incorporation of selenium. Dehydrogenation by selenium dioxide has been noted previously, acetonylacetone giving 1 : 2-diacetylethylene (Armstrong and Robinson, *J.*, 1934, 1650), and ethyl succinate giving the fumarate (Astin, Riley, and Newman, *J.*, 1933, 391), in each case hydrogen atoms being removed from activated methylene groups. In view of the failure of (II*g*) to react with selenium dioxide, where the active methylene group is blocked by substitution, a similar type of reaction appears applicable.

It might be expected that the closest analogy would be provided by the selenium dioxide oxidation of a *cyclo*hexane-1 : 3-dione. As noted above, this has been studied only in the case of 5 : 5-dimethyl*cyclo*hexane-1 : 3-dione, 3 : 3 : 7 : 7-tetramethyl-1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-octahydrophenoxaselenin-1 : 9-dione 10-oxide (anhydromethone selenium oxide) (I*c*) being formed. The generality of the latter reaction has now been shown by the preparation of five more *compounds* of this series, *viz.*, (I*a*), (I*b*), (I*d*), and 2 : 3 : 7 : 8(or 3 : 4 : 6 : 7)-*tetraphenyl*-(I*e* or I*f*) and 2 : 8(or 4 : 6)-*diphenyl*-3 : 3 : 7 : 7-*tetramethyl*-1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-*octahydrophenoxaselenin*-1 : 9-*dione* 10-*oxide* (I*g* or I*h*). These compounds are all golden-yellow and closely resemble that already described (I*c*) in their instability to light and dilute acids, selenium being rapidly deposited. This instability is undoubtedly due to the presence of a double enol ether linkage.

In the formation of these octahydrophenoxaselenin oxide derivatives, dehydrogenation at the reactive methylene group has been accompanied by a union of 2 molecules through the selenium atom. Once again, the presence of a methyl group at position 2 in the diketone molecule interferes with the normal course of oxidation and an attempt to oxidise 5-phenyl-2-methyl*cyclo*hexane-1 : 3-dione led to extensive decomposition. Except, however, for this similarity in the blocking behaviour of a 2-methyl group, the analogy between the oxidation of the diketones and the dioximes cannot be drawn. It may be seen from the analytical data that no union of molecules occurs, and the products arise solely from an intramolecular dehydrogenation process. Further, the properties of the two classes of compound are very different. The red compounds obtained from the dioximes are very stable towards acids and light. They may be crystallised unchanged from a large volume of concentrated hydrochloric acid, without any deposition of selenium. (This behaviour shows that the nitrogen atoms are either not basic, or only extremely weakly so.) They decompose, with deposition of selenium, however, on warming with sodium hydroxide solution.


(III.)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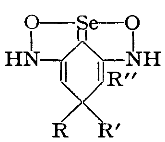
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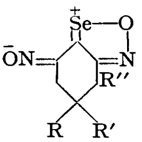
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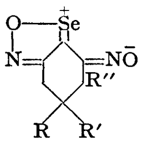
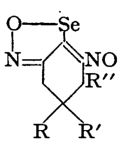

(VII.)


(VIII.)

(*a*, R = R′ = R″ = H; *b*, R = Me, R′ = R″ = H; *c*, R = R′ = Me, R″ = H; *d*, R = Ph, R′ = R″ = H; *e*, R = R″ = Ph, R′ = H; *f*, R = R′ = Me, R″ = Ph.)

The isolation of products containing *gem*-dimethyl groups, *e.g.*, by the oxidation of (II*c*) or (II*f*), indicates that aromatisation of the nucleus has not occurred, and this limits the possible formulæ to (III), (IV), and (V).

Of these formulæ, (V) appears to be excluded by the fact that a Zerewitinoff determination of active hydrogen showed there was none present, while (IV) and (V) scarcely seem feasible on strain considerations. An objection to structure (III) is that the colour is not suggestive of a nitroso-compound, nor could it be induced to react with aniline in glacial acetic acid solution to form an azo-compound.

A preliminary polarographic study was made of (III*a*), obtained from *cyclo*hexane-1 : 3-dione dioxime (see Fig. 1). In phosphate buffer (pH 7·27), a polarographic wave was detected at a half-wave potential of −0·56 volt, with indications of a second wave at −1·64 volts (curve 3). The polarogram was not clear-cut, however, possibly owing to the disturbing influences of selenium on the dropping-mercury electrode. Under other conditions, *e.g.*, in M/20-sodium hydroxide, large erratic maxima were observed doubtless owing to decomposition in the presence of alkali (for explanations of these phenomena, see Kolthoff and Lingane, " Polarography ", Interscience, New York, pp. 113—140). As a comparison, polarograms of *p*-benzoquinone and *p*-nitrosodimethylaniline were made under the same conditions. The quinone, selected because of a formal resemblance to (V), gave a sharp wave at −0·21 volt (curve 2), while the nitroso-compound was reduced at a half-wave potential of −0·59 volt (curve 1). Although it must be emphasised that these results were of a semiquantitative nature only, it is perhaps of significance that the reduction potentials of the nitroso-compound and the organo-selenium compound are so close. Undoubtedly, structure (III) can be considerably modified by resonance between structures (VI), (VII), and (VIII), which could contribute to the stability of this series of compounds.

An examination of the ultra-violet absorption spectra of the compounds obtained from (II*a*) and (II*c*) showed that they were very closely related (see Fig. 2). The former (III*a*) gave maxima at 2270 (9910), 3000 (1450), and 3900 A. (4750), while the latter (III*c*) gave maxima at 2250 (9840), 3000 (1385), and 3900 A. (4650), the figures in parentheses being the values of the molar extinction coefficient ($\varepsilon^{\max.}_{\text{molar}}$). The interpretation of these spectra is complicated by the fact that selenium, when present in an organic molecule, exerts a pronounced bathochromic and hyperchromic effect (Brode, " Chemical Spectroscopy ", Wiley, New York, 1943, p. 260; cf. Behaghel and Schneider, *Ber.*, 1936, **69**, 88; Fisher and Hamer, *Proc. Roy. Soc.*, 1936, **154**, *A*, 703), and no useful deductions have been drawn from these results.

FIG. 1.

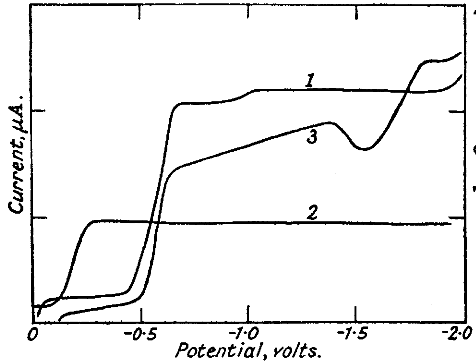
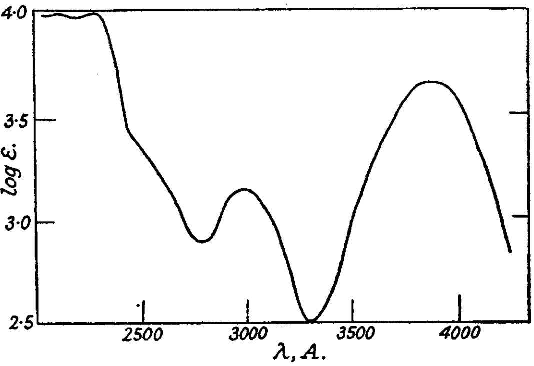


FIG. 2.



In a further attempt to elicit information as to the structure of this series of compounds, the dipole moment of (III*a*) was kindly determined by Mr. R. A. W. Hill at Oxford, who found the value of 2·90 ± 0·03 D. Since, however, the highly polar resonance forms (VI) and (VII) are equally probable and their moments nearly opposed, all the possible formulations could well have a moment of about 3·0 D. Accordingly, it is proposed, tentatively, to name these compounds as derivatives of 7-nitroso-$\Delta^{3:7}$-dihydrobenz-2 : 1 : 3-oxaselenazole (III*a*).

It is intended to continue the study of these interesting compounds.

EXPERIMENTAL.

(All m. p.s are uncorrected.)

7-Nitroso-$\Delta^{3:7}$-dihydrobenz-2 : 1 : 3-oxaselenazole (III*a*).—(i) *cyclo*Hexane-1 : 3-dione [prepared by catalytic reduction of resorcinol in alkaline solution (Hofmann-La Roche; B.P. 416,892; *Chem. Zentr.*, 1935, I, 632; Felton and King, *J.*, 1948, 1371)] was converted into the dioxime (II*a*) (Merling, *loc. cit.*). This substance (7·6 g., 1 mol.) in boiling methanol (50 ml.) was treated with finely powdered selenium dioxide (5·9 g., 1 mol.). A very vigorous reaction ensued, the solution becoming dark red but remaining clear. On cooling, long red needles (5·7 g., 49%) separated, which after recrystallisation from methanol melted at 106° [Found : C, 33·2; H, 2·94; N, 12·8; *M* (Rast), 207; active H (Zerewitinoff), 0. $C_6H_6O_2N_2Se$ requires C, 33·2; H, 2·77; N, 12·9%; *M*, 217]. Light absorption (methanol) : $\lambda_{\max.}$ 2270, 3000, 3900 A.; $\varepsilon_{\max.}$ 9910, 1450, 4750.

(ii) The action of selenium dioxide in acetic anhydride on (II*a*) produced the same red *product*, m. p. 106°, undepressed on admixture with the previous specimen.

7-Nitroso-5-methyl-$\Delta^{3:7}$-dihydrobenz-2 : 1 : 3-oxaselenazole (III*b*).—5-Methyl*cyclo*hexane-1 : 3-dione dioxime (II*b*) (5·9 g.; Vorländer and Kalkow, *loc. cit.*) in boiling methanol (50 ml.) was treated with selenium dioxide (4·65 g., 1 mol.), and on cooling and adding water, the *product* separated as deep orange-red scales (5·4 g., 61%), which after one recrystallisation from aqueous methanol, melted at 91° (Found : C, 36·7; H, 3·47. $C_7H_8O_2N_2Se$ requires C, 36·4; H, 3·46%).

7-Nitroso-5 : 5-dimethyl-$\Delta^{3:7}$-dihydrobenz-2 : 1 : 3-oxaselenazole (III*c*).—(i) 5 : 5-Dimethyl*cyclo*hexane-1 : 3-dione dioxime (II*c*; 2·3 g., from dimedone; Gittel, *loc. cit.*) in boiling methanol (20 ml.) was oxidised with selenium dioxide (1·0 g., 1 mol.). The *product*, precipitated by addition of water, formed long, red needles (2·1 g., 52%), m. p. 109° from aqueous methanol [Found : C, 39·1; H, 4·26; N, 11·7; *M* (Rast), 205. $C_8H_{10}O_2N_2Se$ requires C, 39·2; H, 4·08; N, 11·4%; *M*, 245]. Light absorption (methanol) : $\lambda_{\max.}$ 2250, 3000, 3900 A.; $\varepsilon_{\max.}$ 9840, 1385, 4650.

(ii) A repetition of this experiment using selenium dioxide (2 mols.) gave the same product, m. p. and mixed m. p. 109°, in 58% yield.

7-Nitroso-5-phenyl-$\Delta^{3:7}$-dihydrobenz-2 : 1 : 3-oxaselenazole (III*d*).—5-Phenyl*cyclo*hexane-1 : 3-dione dioxime (II*d*; 1·1 g.; Vorländer, *loc. cit.*) was oxidised in boiling ethanol (15 ml.) with selenium dioxide (0·55 g., 1 mol.). The red crystalline *oxaselenazole* was collected, and on crystallisation from aqueous methanol, formed fine, red needles (1·0 g., 67·5%), m. p. 165° (Found : C, 49·4; H, 3·61. $C_{12}H_{12}O_2N_2Se$ requires C, 49·2; H, 3·41%).

*4 : 5-Diphenyl*cyclo*hexane-1 : 3-dione Dioxime* (II*e*).—4 : 5-Diphenyl*cyclo*hexane-1 : 3-dione (1·4 g.; Borsche, *Ber.*, 1909, **42**, 4498) was converted in the usual manner into the *dioxime*, which crystallised from aqueous ethanol as colourless bunches of needles, m. p. 150° (decomp.) (Found : C, 71·4; H, 5·99.

$C_{18}H_{18}O_2N_2,\frac{1}{2}H_2O$ requires C, 71·3; H, 6·27%. Found, on a sample dried at 120° in a high vacuum : C, 72·2; H, 6·14. $C_{18}H_{18}O_2N_2,\frac{1}{4}H_2O$ requires C, 72·4; H, 6·20%. Further attempts to dehydrate the sample led to decomposition).

7-Nitroso-4 : 5-diphenyl-$\Delta^{3:7}$*-dihydrobenz-2 : 1 : 3-oxaselenazole* (III*e*).—4 : 5-Diphenyl*cyclo*hexane-1 : 3-dione dioxime (II*e*, 0·7 g.) was oxidised in boiling methanol (7 ml.) with selenium dioxide (0·26 g., 1 mol.), and the *product*, collected after careful precipitation with water, crystallised from aqueous methanol as small, red needles (0·55 g., 63%), m. p. 180—181° (Found : C, 58·1; H, 3·61. $C_{18}H_{14}O_2N_2Se$ requires C, 58·5; H, 3·79%).

*4-Phenyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione Dioxime* (II*f*).—4-Phenyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione (3·0 g.; Borsche, *loc. cit.*) was treated for 3 hours under reflux with an ethanolic solution of hydroxylamine (from the hydrochloride, 1·8 g.). The solution was then concentrated to about 10 ml., and water cautiously added until crystallisation commenced. The *dioxime* (2·2 g., 64·5%) was collected and, after several crystallisations from aqueous ethanol, formed rosettes of colourless prisms, m. p. 119—120° (Found : C, 63·5; H, 7·12. $C_{14}H_{18}O_2N_2,H_2O$ requires C, 63·6; H, 7·58%. Found, on a sample dried at 100° in a high vacuum: C, 66·7; H, 7·47. $C_{14}H_{14}O_2N_2,\frac{1}{4}H_2O$ requires C, 67·1; H, 7·39%).

7-Nitroso-4-phenyl-5 : 5-dimethyl-$\Delta^{3:7}$*-dihydrobenz-2 : 1 : 3-oxaselenazole* (III*f*).—4-Phenyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione dioxime (II*f*, 2·0 g.) was oxidised in boiling methanol (25 ml.) with selenium dioxide (0·9 g., 1 mol.), and the *product*, precipitated by the addition of water, crystallised from aqueous methanol, forming red rhombs, m. p. 137° (Found : C, 52·7; H, 4·66. $C_{14}H_{14}O_2N_2Se$ requires C, 52·3; H, 4·36%).

*5-Phenyl-2-methyl*cyclo*hexane-1 : 3-dione Dioxime* (II*g*).—5-Phenyl-2-methyl*cyclo*hexane-1 : 3-dione (1·1 g.; Mattar, Hastings, and Walker, *J.*, 1930, 2455) was treated with an ethanolic solution of hydroxylamine (from the hydrochloride, 1·08 g., 2 mols.). The mixture, after refluxing on the water-bath for 2 hours, was evaporated to small volume, and water added until crystallisation was initiated. The *dioxime* (0·8 g., 63%) formed colourless needles from aqueous ethanol, m. p. 188° (efferv.) (Found : C, 67·7; H, 6·94. $C_{13}H_{16}O_2N_2$ requires C, 67·2; H, 6·90%). Attempted oxidation of this dioxime by means of selenium dioxide in boiling methanol, under the conditions described above, was unsuccessful, some decomposition being observed. The bulk (approx. 85%) of the dioxime was recovered unchanged, m. p. 188° (efferv.) undepressed on admixture with an authentic specimen.

1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-Octahydrophenoxaselenin-1 : 9-dione 10-Oxide (I*a*).—*cyclo*Hexane-1 : 3-dione (6·0 g.) in hot methanol (20 ml.) was oxidised with selenium dioxide (3·75 g., 1 mol.); a vigorous reaction ensued, giving a dark yellow solution from which, on cooling, golden-yellow, shining crystals (6·2 g., 77·5%) were obtained. On recrystallisation from methanol, *1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-octahydrophenoxaselenin-1 : 9-dione 10-oxide* formed golden-yellow needles, m. p. 180° (decomp.) (Found : C, 48·3; H, 4·2. $C_{12}H_{12}O_4Se$ requires C, 48·1; H, 4·0%). This substance decomposes on prolonged exposure to daylight, or on warming with dilute mineral acid, with deposition of selenium as a red powder.

3 : 7-Dimethyl-1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-octahydrophenoxaselenin-1 : 9-dione 10-Oxide (I*b*).—5-Methyl*cyclo*hexane-1 : 3-dione (1·3 g.) in hot methanol (20 ml.) was oxidised by selenium dioxide (1·2 g.), and on cooling the *oxide* crystallised. After recrystallisation from ethyl acetate, it formed glittering, golden scales, m. p. 185° (decomp.), containing solvent of crystallisation (Found : C, 51·9, 52·0; H, 5·49, 5·45. $C_{14}H_{16}O_4Se,\frac{1}{2}C_4H_8O_2$ requires C, 51·8; H, 5·40%). Attempted removal of the solvent led to decomposition.

3 : 7-Diphenyl-1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-octahydrophenoxaselenin-1 : 9-dione 10-Oxide (I*d*).—5-Phenyl*cyclo*hexane-1 : 3-dione (1·0 g.) was oxidised in the usual manner with selenium dioxide (0·6 g., 1 mol.) in hot methanol. Recrystallised from benzene–ethanol, the *oxide* formed glittering, golden plates, m. p. 187—188° (with reddening, Se?) (Found : C, 64·0; H, 4·64. $C_{24}H_{20}O_4Se$ requires C, 63·9; H, 4·43%).

2 : 3 : 7 : 8 (or 3 : 4 : 6 : 7)-Tetraphenyl-1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-octahydrophenoxaselenin-1 : 9-dione 10-Oxide (I*e* or I*f*).—4 : 5-Diphenyl*cyclo*hexane-1 : 3-dione (0·8 g.) was oxidised in methanol by selenium dioxide (0·34 g., 1 mol.). The *product*, precipitated on addition of a little water, formed very small pale yellow needles, m. p. 164° (decomp.), on crystallisation from aqueous methanol (Found : C, 67·9; H, 5·02. $C_{36}H_{28}O_4Se,2H_2O$ requires C, 67·6; H, 5·01%). Attempts to dehydrate the sample led to decomposition with liberation of selenium.

2 : 8 (or 4 : 6)-Diphenyl-3 : 3 : 7 : 7-tetramethyl-1 : 2 : 3 : 4 : 6 : 7 : 8 : 9-octahydrophenoxaselenin-1 : 9-dione 10-Oxide (I*g* or I*h*).—4-Phenyl-5 : 5-dimethyl*cyclo*hexane-1 : 3-dione (1·0 g.) in hot methanol was oxidised as above with selenium dioxide (0·37 g.), and the *product* precipitated by dropwise addition of water. It crystallised from aqueous methanol as microscopic, primrose-yellow needles, m. p. 133° (Found : C, 66·6; H, 5·81. $C_{28}H_{28}O_4Se$ requires C, 66·3; H, 5·52%).

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