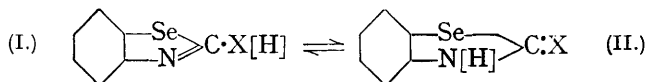


#### 414. The Unsaturation and Tautomeric Mobility of Heterocyclic Compounds. Part VII. Selenazole Derivatives.

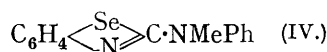
By CHIRAGH HASAN and ROBERT F. HUNTER.

As might be anticipated from the theory of sextuple valency group stability and the striking resemblance of selenophen to thiophen in chemical properties (Briscoe and Peel, J., 1928, 1741), semi-cyclic triad systems containing a selenazole ring ( $I \rightleftharpoons II$ ) exhibit the closest similarity to their thiazole analogues (Hunter, J., 1926, 1385; 1930, 125) in behaviour.

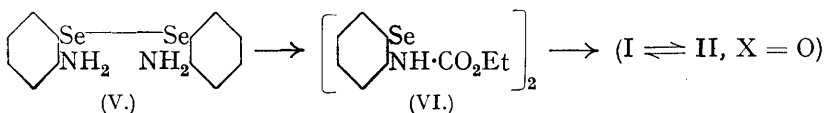


It was not possible to apply the symmetry test of mobility to 1-aminobenzselenazole ( $I \rightleftharpoons II$ ,  $X = NH$ ), which was readily obtained from phenylselenourea (Stolte, Ber., 1886, 19, 2350) by treatment with bromine, on account of repeated failures to isolate *as.*-phenylacetylselenourea, which apparently undergoes immediate isomerisation to the stable isomeride under the conditions of acetylation (cf. Hegershoff, Ber., 1899, 32, 3649; Wheeler, Amer. Chem. J., 1902, 27, 270; Hunter and Pride, J., 1929, 944). On methylation, the amidine yielded 1-imino-2-methyl-1 : 2-dihydrobenzselenazole, which may have been accompanied by a small amount of the isomeric 1-methylaminobenzselenazole; this was rationally synthesised from *s*-phenylmethylselenourea. On acetylation with acetic anhydride, 1-aminobenzselenazole yielded 1-acetamidobenzselenazole, identical with that obtained from *s*-phenylacetylselenourea and bromine. The presence of a  $\mu$ -amino-group in the base was also established by the formation of an unstable diazonium chloride, which yielded 1-chlorobenzselenazole on being heated with hydrochloric acid (cf. Hunter and Jones, J., 1930, 2190).

Substitution of phenyl for a hydrogen atom of the 1-amino-group stabilises the imino-dihydro-form of the triad system, and the methylation of 1-anilinobenzselenazole ( $I \rightleftharpoons II$ ,  $X = NPh$ ) gave rise to a mixture of 1-phenylimino-2-methyl-1 : 2-dihydrobenzselenazole (III) and 1-phenylmethylaminobenzselenazole (IV), in which the former isomeride, derived from the amino-aromatic form, was present in larger amount.



1-Hydroxybenzselenazole ( $I \rightleftharpoons II$ ,  $X = O$ ) was obtained both by phosgenation of the zinc salt of *o*-aminoselenophenol and by hydrolysis of 1-chlorobenzselenazole. It was most conveniently prepared by reducing *bis*-*o*-urethanophenyl diselenide (VI), obtained by condensation of *bis*-*o*-aminophenyl diselenide (V) with ethyl chloroformate, with tin and hydrochloric acid.

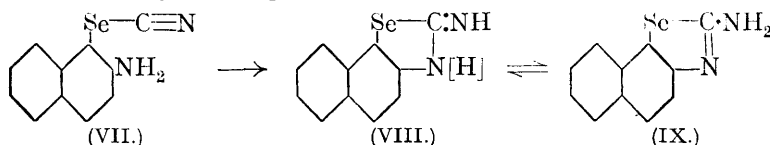


On methylation in an alkaline medium it yielded 1-keto-2-methyl-1 : 2-dihydrobenzselenazole, the constitution of which follows from its synthesis from 1-imino-2-methyl-1 : 2-dihydrobenzselenazole by Besthorn's method (Ber., 1910, 43, 1523).

1-Thiolbenzselenazole ( $I \rightleftharpoons II$ ,  $X = S$ ) was prepared from the zinc salt of *o*-aminoselenophenol and thiocarbonyl chloride and by the action of sodium hydrosulphide on 1-chlorobenzselenazole. A more satisfactory method of preparation consisted, however, in heating *bis*-*o*-nitrophenyl diselenide with a mixture of sodium disulphide, carbon disulphide, and aqueous sodium hydroxide in the presence of hydrogen sulphide, the mechanism of the reaction presumably consisting in reduction of the nitro-derivative to the aminoselenophenol and the subsequent condensation of this with carbon disulphide

(cf. Hofmann, *Ber.*, 1887, **20**, 1788). Methylation of the thiol-selenazole yielded an oily product, which appeared to be the expected S-methyl derivative, since it differed from 1-thio-2-methyl-1 : 2-dihydrobenz-selenazole synthesised from the corresponding ketomethyl-dihydroselenazole and phosphorus pentasulphide.

In an attempt to prepare 1-bromo- $\beta$ -naphthylthiourea by heating a mixture of the hydrochloride of 1-bromo- $\beta$ -naphthylamine and aqueous potassium thiocyanate, it was discovered that the reaction took quite another course with the direct production of 1-amino- $\alpha$ -naphthathiazole (unpublished result). A similar reaction between the bromo-naphthylamine and potassium selenocyanate provides a convenient synthesis of 1-amino- $\alpha$ -naphthaselenazole (VIII  $\rightleftharpoons$  IX). Since it was not found possible to prepare selenoureas by heating aqueous solutions of salts of arylamines with potassium selenocyanate, the mechanism of the reaction presumably consists in substitution of a selenocyano-group for  $\alpha$ -bromine, and subsequent interaction of this with the amino-group in the *o*-position to give 1-imino-1 : 2-dihydro- $\alpha$ -naphthaselenazole (VIII).



The interaction of *s*-phenyl- $\beta$ -naphthylselenourea with bromine was similar to that of the sulphur analogue and gave rise to 1-anilino- $\alpha$ -naphthaselenazole, the constitution of which follows from its degradation to a bisaminonaphthyl diselenide, identical with that obtained from 1-amino- $\alpha$ -naphthaselenazole on alkali fusion.

#### EXPERIMENTAL.

Phenylimidocarbonyl chloride was prepared by the action of chlorine upon phenylthiocarbimide in carbon tetrachloride (Perkin and Lewis, *J. Amer. Chem. Soc.*, 1922, **44**, 2897), the fraction, b. p. 205—206°, being separately collected. When chloroform was used as a diluent (Sell and Zierold, *Ber.*, 1874, **7**, 1229), nuclear substitution occurred, even in a freezing mixture; the product distilled at 195—250°.

Phenylselenocarbimide was prepared by treating phenylimidocarbonyl chloride (13.2 g.) in an equal volume of ether with sodium selenide (11 g.), the mixture being kept for 2 days and then extracted with ether. The brown oil obtained contained phenyliminocarbonyl chloride, but this did not interfere in the condensation of the selenocarbimide with amines. The pure selenocarbimide was isolated by distillation in a vacuum (b. p. 120—130°/6—8 mm.), but there was considerable decomposition. After a week, phenylselenocarbimide deposited large brown needles and small white crystals, but the product from which these had been removed behaved in the same way as freshly prepared specimens and yielded the expected selenoureas on treatment with amines.

Phenylselenourea was obtained by treating a solution of the selenocarbimide (20 g.) in benzene with excess of aqueous ammonia (*d* 0.880). On recrystallisation from alcohol and thereafter from benzene, it formed needles, m. p. 182° (to a black liquid which became yellow at 216—218°) (Found : Se, 39.5. Calc. : Se, 39.7%). The compound became pink and thereafter grey on keeping, the changes being largely dependent on the extent of exposure to light. A dark grey specimen which had been kept for 5 months behaved normally on treatment with bromine and yielded 1-aminobenz-selenazole.

1-Aminobenz-selenazole (I  $\rightleftharpoons$  II; X = NH).—A suspension of finely powdered phenylselenourea (13 g.) in carbon tetrachloride (60 c.c.) and chloroform (10 c.c.) was stirred during the addition of bromine (3.7 c.c. in 5 c.c. of carbon tetrachloride); heat was evolved. The mixture was heated under reflux until the evolution of hydrogen bromide abated; the insoluble product was collected, crushed, dried in a vacuum, and gradually added to saturated sulphurous acid (150 c.c.). The mixture was treated with sulphur dioxide for 15 minutes, warmed to 50—60°, again treated with sulphur dioxide, and heated to boiling; the greater part of the product then dissolved. The fluorescent filtrate on basification with aqueous ammonia (*d* 0.880) yielded the base partly in colourless needles and partly as a pinkish gummy precipitate which subsequently solidified. Recrystallisation from water or alcohol gave pink crystals. 1-Aminobenz-selenazole was best purified by filtering a hot solution of the base in benzene into petrol;

it then crystallised in colourless needles, m. p. 142° (Found: C, 42.7; H, 3.0; Se, 39.9.  $C_7H_6N_2Se$  requires C, 42.6; H, 3.0; Se, 40.0%). Cyclisation of phenylselenourea in chloroform proved unsatisfactory, and bromine in excess of the calculated amount caused nuclear substitution.

**Methylation of 1-Aminobenzselenazole.**—A mixture of the base (0.5 g.), methyl alcohol (10 c.c.), and methyl sulphate (14 c.c.) was heated on a water-bath for 2 hours, cooled, treated with excess of alkali, and again heated. The yellow oil was separated, dried in a vacuum, and extracted with benzene. The gum obtained commenced to solidify in a vacuum after a fortnight, yielding small yellow crystals of 1-imino-2-methyl-1:2-dihydrobenzselenazole, m. p. 104° (Found: Se, 37.2.  $C_8H_8N_2Se$  requires Se, 37.4%); a second crop of crystals of the same base subsequently separated. By methylation of the aminoselenazole (2.0 g.) with methyl iodide (1.5 c.c.) at 100° for 10 hours, a similar gum was obtained, from which the iminomethyldihydrobase was isolated. 1-Nitrosoimino-2-methyl-1:2-dihydrobenzselenazole, obtained by treating a solution of the iminomethyldihydrobenzselenazole (3 g.) in glacial acetic acid (11 c.c.) with sodium nitrite (1.1 g. in 2.5 c.c. of water) at 7–8°, formed brown microscopic crystals, which exploded at 142–144° after being dried in a vacuum (Found: Se, 32.6.  $C_8H_7ON_3Se$  requires Se, 32.9%).

**Synthesis of 1-Methylaminobenzselenazole.**—An aqueous solution of methylamine (33%) was added drop by drop to a solution of pure phenylselenocarbimide (5 g.) in benzene (15 c.c.) until the odour of the carbimide disappeared (about 5.5 c.c.); the gum obtained by evaporation of the solvent in a vacuum was rubbed. *s*-Phenylmethylselenourea formed colourless prisms, which turned pink and thereafter grey on keeping, m. p. 111° (Found: Se, 36.7.  $C_8H_{10}N_2Se$  requires Se, 37.1%). A suspension of the selenourea (3 g.) in carbon tetrachloride (20 c.c.) and chloroform (10 c.c.) was treated with bromine (0.8 c.c. in 2 c.c. of chloroform), hydrogen bromide being evolved. The mixture was heated under reflux, and the yellow product dissolved in sulphurous acid. On basification, 1-methylaminobenzselenazole separated as a pink crystalline precipitate, which formed colourless needles, m. p. 140°, on recrystallisation from benzene (Found: Se, 37.1.  $C_8H_8N_2Se$  requires Se, 37.4%).

**Acetylation of 1-Aminobenzselenazole and the Synthesis of 1-Acetamidobenzselenazole.**—(i) The solution obtained by warming 1-aminobenzselenazole (1.2 g.) with acetic anhydride (3 c.c.) set to a crystalline mass on cooling; the excess of acetic anhydride was destroyed by treatment with water. On recrystallisation 1-acetamidobenzselenazole was obtained in needles and also in thick cubes, m. p. 190° (Found: Se, 32.7.  $C_9H_8ON_2Se$  requires Se, 33.05%). The mother-liquor furnished a substance of unknown nature, which crystallised in needles, m. p. 130°. (ii) Attempts to prepare labile acetylphenylselenourea by acetylation of phenylselenourea with acetic anhydride at 80° (cf. Hegershoff, *loc. cit.*) gave *s*-acetylphenylselenourea, which separated from ethyl acetate in light brown plates, m. p. 195° (Found: Se, 32.6.  $C_9H_{10}ON_2Se$  requires Se, 32.8%). When a suspension of this (0.9 g.) in carbon tetrachloride (10 c.c.) was treated with bromine (0.3 c.c. in 1.5 c.c. of chloroform), and the mixture heated, hydrogen bromide was evolved after 3 minutes. Basification of the filtrate from the sulphurous acid reduction gave 1-acetamidobenzselenazole, m. p. and mixed m. p. with (i) 190°. *s*-Diphenylselenourea, obtained by condensation of phenylselenocarbimide and aniline in benzene, crystallised from alcohol in plates, m. p. 192–194° (to a black liquid which became yellow at 216–218°) (Found: Se, 28.4. Calc.: Se, 28.7%). Stolte (*loc. cit.*) gives m. p. 186°.

**1-Anilinobenzselenazole** ( $I \rightleftharpoons II$ ;  $X = NPh$ ).—Diphenylselenourea (8 g.) in carbon tetrachloride (40 c.c.) and chloroform (20 c.c.) was cyclised with bromine (1.8 c.c.), and the resulting oil treated with sulphurous acid. 1-Anilinobenzselenazole crystallised from alcohol in needles, m. p. 170° (Found: C, 57.3; H, 3.6; Se, 28.7.  $C_{13}H_{10}N_2Se$  requires C, 57.1; H, 3.6; Se, 28.9%). The *picrate* crystallised in yellow needles, m. p. 245° (Found: Se, 15.3.  $C_{13}H_{10}N_2Se, C_6H_3O_7N_3$  requires Se, 15.7%).

**Methylation of 1-Anilinobenzselenazole.**—A mixture of 1-anilinobenzselenazole (1 g.), methyl alcohol (15 c.c.), and methyl sulphate (4.3 c.c.) was heated for 2 hours and then boiled with aqueous sodium hydroxide (25%). The oil obtained was dissolved in acetone and treated with picric acid (1.5 g.). The *picrate*, which formed yellow needles, m. p. 200°, on recrystallisation from acetone and thereafter from benzene, was identified as that of 1-phenylmethylaminobenzselenazole by mixed m. p. with the specimen synthesised from 1-thiolbenzselenazole and methylaniline (Found: Se, 15.1.  $C_{14}H_{12}N_2Se, C_6H_3O_7N_3$  requires Se, 15.3%). The acetone mother-liquor on concentration furnished the *picrate* of 1-phenylimino-2-methyl-1:2-dihydrobenzselenazole (about 75% of the total *picrate*), m. p. 172° on recrystallisation (Found: Se, 15.1%).

*Synthesis of 1-Phenylmethylaminobenzselenazole.*—A mixture of 1-thiolbenzselenazole (0.5 g.) and methylaniline (0.3 g.) was heated at 170–180° for 6 hours, hydrogen sulphide being evolved. The ethereal extract of the product was washed with aqueous sodium hydroxide, and the gum obtained by removal of the ether was dissolved in benzene and converted into the picrate, which was undepressed in m. p. by admixture with the specimen obtained from the methylated anilino-base.

A more convenient method than Bauer's (*Ber.*, 1913, 46, 94) for the preparation of bis-*o*-nitrophenyl diselenide is treatment of an alcoholic solution of *o*-nitrophenyl selenocyanate with small pieces of sodium; the diselenide is precipitated and on recrystallisation from benzene forms brown needles, m. p. 209°.

Bis-*o*-aminophenyl diselenide was conveniently prepared by the following modification of Bauer's method: a mixture of the bisnitrophenyl diselenide (10 g.), sodium hydrosulphide (10 g.), and alcohol (50 c.c.) was heated under reflux for  $\frac{1}{2}$  hour. The solution was diluted with water and oxidised with hydrogen peroxide; the precipitated diselenide crystallised from alcohol in brown plates, m. p. 80°.

*1-Hydroxybenzselenazole* ( $I \rightleftharpoons II$ ;  $X = O$ ).—(i) *Condensation of bis-*o*-aminophenyl diselenide with ethyl chloroformate.* The powdered diselenide (8 g.) was treated with ethyl chloroformate (6.5 c.c.), the mixture kept for 10 minutes and then heated on a water-bath, and the product recrystallised from alcohol, *bis-*o*-urethanophenyl diselenide* being obtained in brown needles, m. p. 110° (Found: Se, 32.2.  $C_{18}H_{20}O_4N_2Se_2$  requires Se, 32.5%). This derivative (4 g.) was heated with granulated tin (6 g.) and concentrated hydrochloric acid (30 c.c.) under reflux for 20 minutes; the filtered solution, on cooling, deposited *1-hydroxybenzselenazole*, which crystallised from alcohol in needles, m. p. 140° (Found: C, 42.2; H, 2.7; Se, 39.8.  $C_7H_5ONSe$  requires C, 42.4; H, 2.5; Se, 39.9%).

(ii) *Phosgenation of the zinc salt of *o*-aminoselenophenol.* A solution of bis-*o*-aminophenyl diselenide (8 g.) in hot alcohol was treated with concentrated hydrochloric acid (30 c.c.) and the mixture was diluted with water (15 c.c.), warmed, treated with zinc dust (8–10 g.), and boiled until the precipitated hydrochloride dissolved. The yellow filtrate from the mixture was treated with concentrated aqueous sodium acetate; the yellow zinc salt of *o*-aminoselenophenol thus obtained became black on keeping. The zinc salt (1.2 g.) was boiled under reflux with a 12% solution of carbonyl chloride in toluene (20 c.c.) for 2–3 hours, the toluene removed by evaporation, and the gummy product extracted with ether. On removal of ether, 0.15 g. of *1-hydroxybenzselenazole* was obtained, m. p. 138°, which was identified by a mixed m. p. determination with the specimen already described.

(iii) *Hydrolysis of 1-chlorobenzselenazole.* 1-Aminobenzselenazole (5 g.) in concentrated hydrochloric acid (10 c.c.) and water (20 c.c.) was diazotised with sodium nitrite (3 g.), concentrated hydrochloric acid (30 c.c.) added, and the mixture boiled. On distillation in steam, 1-chlorobenzselenazole passed over as a reddish oil, which was extracted in ether (yield, 2–3%). When a solution of this (0.2 g.) in alcohol (15 c.c.) was heated under reflux for 48 hours and concentrated, *1-hydroxybenzselenazole* was obtained; it was identified by m. p. and mixed m. p. determination with the specimen (i).

*Methylation.* A solution of *1-hydroxybenzselenazole* (1.5 g.) in aqueous sodium hydroxide (25%; 13 c.c.) and chloroform (5 c.c.) was treated with methyl sulphate (6.5 c.c.), and after 20 minutes the mixture was heated on a water-bath for an hour. The oil obtained, after destruction of the excess of methyl sulphate with alkali and removal of chloroform, partly crystallised in 2 days. On recrystallisation from benzene, *1-keto-2-methyl-1:2-dihydrobenzselenazole* was obtained in thick plates, m. p. 60° (Found: Se, 36.9.  $C_8H_7ONSe$  requires Se, 37.2%).

*Synthesis of 1-Keto-2-methyl-1:2-dihydrobenzselenazole.*—A solution of nitrosoimino-2-methyl-1:2-dihydrobenzselenazole (1 g.) in xylene (15 c.c.) was heated until it was almost colourless. The gum remaining after removal of the xylene was dissolved in benzene and the solution was decolorised (charcoal) and concentrated. The oil obtained crystallised after 2 days, giving thick plates, m. p. 58–60° alone and when mixed with the preceding specimen.

*1-Thiolbenzselenazole* ( $I \rightleftharpoons II$ ;  $X = S$ ).—(i) *Condensation of nascent *o*-aminoselenophenol with carbon disulphide.* Hydrogen sulphide was passed through a mixture of bis-*o*-nitrophenyl diselenide (2 g.), sodium hydrosulphide (5 g.), sodium hydroxide (5 g.), water (50 c.c.), and carbon disulphide (10 c.c.), heated under reflux until the diselenide dissolved; heating was then continued for an hour. After 12 hours' cooling, *1-thiolbenzselenazole* separated; it crystallised from alcohol in flat needles, m. p. 159° (Found: C, 39.5; H, 2.4; Se, 36.7.  $C_7H_5NSSe$  requires C, 39.2; H, 2.3; Se, 36.9%).

(ii) *Condensation of the zinc salt of *o*-aminoselenophenol with thiocarbonyl chloride.* The zinc



salt (0.4 g.) was added to a suspension of thiocarbonyl chloride (1 c.c.) in chloroform (15 c.c.) and water (20 c.c.), and the mixture shaken at intervals for more than an hour; most of the zinc salt had then dissolved. Partial separation of the chloroform layer and evaporation of the solvent yielded 1-thiolbenzselenazole, m. p. 159° alone and when mixed with the specimen already described. In another experiment, the original solution was evaporated, and the residue extracted with hot aqueous alkali; on acidification 1-thiolbenzselenazole was obtained, m. p. 159° after recrystallisation.

(iii) *Synthesis from 1-chlorobenzselenazole and sodium hydrosulphide.* The solution obtained by heating the chloroselenazole with sodium hydrosulphide in alcoholic solution for 2 hours was evaporated to dryness. An aqueous extract of the residue on acidification furnished a precipitate, which on extraction with alcohol yielded 1-thiolbenzselenazole, m. p. 154°, and 158° when mixed with the specimen (i).

*Methylation.* A solution of 1-thiolbenzselenazole (1.5 g.) in methyl alcohol (10 c.c.) and methyl sulphate (5 c.c.) was heated under reflux for 2 hours and cooled, and the excess of methyl sulphate destroyed with aqueous ammonia ( $d$  0.880). After extraction with chloroform and washing of the extract with water, a pale yellow oil was obtained, which was dried in a vacuum for a fortnight (Found: Se, 34.4.  $C_8H_7NSe$  requires Se, 34.6%). An alcoholic solution of this gave with aqueous mercuric chloride an addition compound, which crystallised from benzene in yellow needles, m. p. 208° (decomp.).

*Synthesis of 1-Thio-2-methyl-1:2-dihydrobenzselenazole.*—An intimate mixture of 1-keto-2-methyl-1:2-dihydrobenzselenazole (0.5 g.) and phosphorus pentasulphide (2 g.) was heated in an oil-bath at 130–140° for 4 hours, and the product extracted with hot benzene. Removal of the benzene yielded a gum, which was dissolved in methyl alcohol; after 2 days, 1-thio-2-methyl-1:2-dihydrobenzselenazole separated in rhombic crystals, which were crushed on porous earthenware and dried in a vacuum; m. p. 80° (Found: Se, 34.4.  $C_8H_7NSe$  requires Se, 34.6%).

#### *$\alpha$ -Naphthaselenazoles.*

*1-Amino- $\alpha$ -naphthaselenazole.*—1-Bromo- $\beta$ -naphthylamine hydrochloride (51 g.) in alcohol (about 100 c.c.) was treated with a solution of potassium selenocyanate (28 g.) in water (80 c.c.); the mixture was kept for 12 hours and evaporated to dryness on a water-bath. The residue was extracted with boiling water and the crystalline salts of the aminoselenazole were basified with ammonia. On recrystallisation from alcohol, the *selenazole* was obtained in lustrous plates, m. p. 252° (Found: C, 53.5; H, 3.4; Se, 31.7.  $C_{11}H_8N_2Se$  requires C, 53.5; H, 3.2; Se, 32.0%). The amino-base gradually developed a pink colour. On diazotisation it gave a diazonium salt which coupled with  $\alpha$ -naphthol, yielding a red azo-dye. The *acetyl* derivative, obtained by treatment with acetic anhydride, separated from alcohol in plates, m. p. 250° (Found: Se, 27.2.  $C_{13}H_{10}ON_2Se$  requires Se, 27.2%).

*Bis-2-amino- $\alpha$ -naphthyl Diselenide.*—An intimate mixture of 1-amino- $\alpha$ -naphthaselenazole (5 g.) and sodium hydroxide (6 g.) was fused by heating in an oil-bath, and the cooled melt was extracted with ice-water, leaving a residue of  $\beta$ -naphthylamine. The aqueous alkaline extract on exposure to air deposited the *diselenide* in microscopic needles, which on recrystallisation formed brown plates, decomp. about 120° after softening at 80° (Found: Se, 35.3.  $C_{20}H_{16}N_2Se_2$  requires Se, 35.7%).

*s-Phenyl- $\beta$ -naphthylselenourea*, prepared from  $\beta$ -naphthylamine and phenylselenocarbimide in benzene, formed a granular mass, which was purified by extraction with alcohol and benzene; m. p. 174° (Found: Se, 24.1.  $C_{17}H_{14}N_2Se$  requires Se, 24.3%).

*1-Anilino- $\alpha$ -naphthaselenazole.*—A suspension of the phenylnaphthylselenourea (3.2 g.) in carbon tetrachloride (30 c.c.) and chloroform (10 c.c.) was cyclised with bromine (0.6 c.c. in 1 c.c. of carbon tetrachloride), and the product treated with sulphurous acid. On basification, 1-anilino- $\alpha$ -naphthaselenazole was obtained; it separated from ethyl acetate in needles, m. p. 210° (Found: C, 63.4; H, 3.8; Se, 24.15.  $C_{17}H_{13}N_2Se$  requires C, 63.15; H, 3.7; Se, 24.4%). On fusion with sodium hydroxide this base also yielded bis-2-amino- $\alpha$ -naphthyl diselenide and  $\beta$ -naphthylamine.

*1-Thiol- $\alpha$ -naphthaselenazole* was obtained by heating a mixture of bis-2-amino- $\alpha$ -naphthyl diselenide, sodium hydrosulphide, aqueous sodium hydroxide, and carbon disulphide in a stream of hydrogen sulphide. On recrystallisation from alcohol it formed yellow needles, m. p. 228° (Found: Se, 29.5.  $C_{11}H_7NSe$  requires Se, 29.9%).