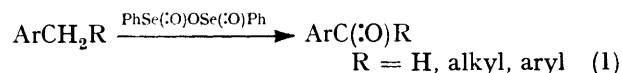


## Oxidation of Benzylic Hydrocarbons with Benzeneseleninic Anhydride and Related Reactions

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The use of benzeneseleninic anhydride as a new side-chain oxidant for a variety of aromatic and heteroaromatic hydrocarbons has been investigated. The oxidation normally proceeds well for simple substrates, neat or in chlorobenzene solution at 100–130 °C. In examples where the aromatic rings are susceptible towards electrophilic attack selenated compounds are usually formed as the major by-products.

ALTHOUGH several useful methods<sup>1</sup> exist for the direct oxidation of benzylic hydrocarbons to aldehydes or ketones new methodology is always welcome. The special oxidizing properties<sup>2</sup> associated with benzeneseleninic anhydride, PhSe(:O)OSe(:O)Ph, suggested that this might be a useful and new reagent to effect these transformations.



Attempted oxidation of toluene by the anhydride at reflux temperatures failed. However, when heated in a sealed tube at 120 °C for an extended period of time (1 week) benzaldehyde and some benzoic acid were produced in low yield. It was found convenient in this and later reactions to isolate the aldehydes as their 2,4-dinitrophenylhydrazone derivatives. Similar oxidation of *o*-xylene proceeded much more readily and gave *o*-tolualdehyde after 16 h at 120 °C. The yield of aldehyde here was equivalent to 0.6 mol for every mole of benzeneseleninic anhydride used. *o*-Toluic acid was also obtained in *ca.* equal amounts together with near quantitative formation of diphenyl diselenide. It was clear that water was also being produced during the reaction. During these reactions the acid was produced from the aldehyde by further oxidation with the anhydride or some other reactive selenium species. Thus, in separate experiments, benzaldehyde with the anhydride did indeed yield benzoic acid while in the control reaction (*i.e.* when PhCHO was heated alone) no acid was produced.

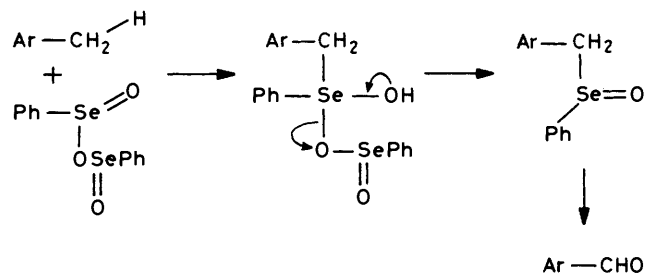
Reaction of *p*-xylene with the anhydride gave *p*-tolualdehyde in reasonable yields (62–72%) with some *p*-toluic acid (*ca.* 30%) and diphenyl diselenide (97%). The diselenide produced in this and later reactions could be readily recovered and reoxidized to benzeneseleninic anhydride.<sup>3</sup>

Although ceric ammonium nitrate<sup>1b</sup> is a superior reagent for the oxidation of toluenes and xylenes to aldehydes the anhydride was noticeably better than selenium dioxide in similar transformations.<sup>1a,c</sup>

We next turned our attention to the oxidation of more substituted methylarenes with the anhydride. While *p*-nitrotoluene failed to react under a variety of conditions, *p*-methoxytoluene reacted readily and at a rate noticeably faster than that with the xylenes. Although *p*-methoxybenzaldehyde was invariably formed together

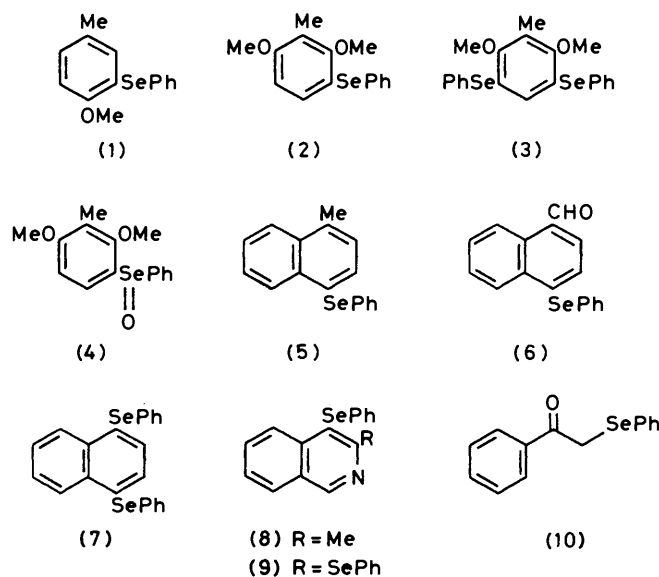
with some *p*-methoxybenzoic acid the major product (up to 40%) was the selenenyl-benzene (1). As with the reactions with the xylenes it was found advantageous to perform these reactions in sealed tubes to avoid loss of volatile components.

A mechanism which could account for the formation of the various aldehydes is shown in the Scheme and in-



SCHEME

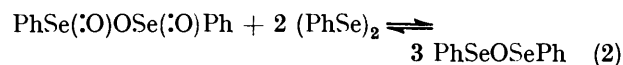
volves initial benzeneseleninylation followed by Pummerer-like rearrangement. Ample literature precedence exists for the Pummerer reaction of selenoxides at temperatures in excess of 100 °C.<sup>4</sup> The formation of the selenide (1) during the reaction of *p*-methoxytoluene with the anhydride will be discussed later. Reaction of 9,10-dimethylantracene with 2 equiv. of the anhydride



in chlorobenzene at 100 °C gave a 56% yield of 9-formyl-10-methylanthracene and 18% of 9,10-diformylanthracene. Reaction of 9,10-dimethylanthracene for extended periods of time (20 h) afforded anthraquinone in 64% yield.

Reaction of 1,3-dimethoxy-2-methylbenzene with the anhydride was slower than with *p*-methoxytoluene and even after 17 h at 110 °C no aldehydes or acidic products were obtained. Instead, the selenenyl-benzene (2) was formed in 49% yield when 0.33 mol equiv. of the anhydride were used. Increasing the proportion of anhydride to 1 equiv. gave compound (2) in 85% yield together with a small quantity (5%) of another product which was shown to be the selenenyl-benzene (3).

The high yield of selenated products obtained during these reactions implied that the oxygen atoms initially associated with the anhydride were being lost in some way. A possible selenating reagent formed during the reaction could be PhSeOSePh. Accordingly, when benzeneseleninic anhydride (1/3 equiv.) was equilibrated with diphenyl diselenide (2/3 equiv.) as in equation (2),



and this mixture was used as a reagent with 1,3-dimethoxy-2-methylbenzene, a 91% yield of compound (2) was obtained. In contrast, with only diphenyl diselenide present no reaction resulted while the use of benzeneselenenyl chloride in benzene at reflux only 6% of compound (2) was obtained.

It was suspected that 1,3-dimethoxy-2-methylbenzene was also undergoing seleninylation and that the intermediate selenoxide was decomposing by loss of oxygen to afford compound (2). In order to test this hypothesis compound (2) was oxidized to the selenoxide (4) by treatment with H<sub>2</sub>O<sub>2</sub> and heated in chlorobenzene for 18.5 h. After this time compound (2) could be isolated in 49% yield together with *ca.* 40% of unchanged selenoxide (4). When the reaction was repeated with 1 mol equiv. of diphenyl diselenide a quantitative yield of compound (2) was obtained after only 8 h. Other examples of selenoxides that decomposed upon heating to give oxygen and selenides have been reported.<sup>6</sup> The formation of the selenide (1) as the major product upon oxidation of *p*-methoxytoluene with benzeneseleninic anhydride may also, at least in part, be due to similar processes.

Treatment of an excess of 1-methylnaphthalene with the anhydride neat at 120 °C gave, in addition to 1-naphthaldehyde (37%), the selenenyl-naphthalene (5) (32%), and the selenenyl-naphthaldehyde (6) (2%).

The yields here were based on the amount of 1-methylnaphthalene being consumed. In another experiment in a sealed tube one further product was isolated in low yield (6%) and shown to be the diselenenyl-naphthalene (7). By varying the amount of anhydride and reaction times it was not possible to improve substantially the yield of 1-naphthaldehyde.

The structure of compound (5) was entirely consistent

with its spectral data, but it was also prepared independently by treatment of 1-methyl-4-naphthylmagnesium bromide with benzeneselenenyl chloride. The structures of compounds (6) and (7) also follow from their spectral properties. The key features being resonances in the <sup>1</sup>H n.m.r. spectra at δ 8.28 (dd, *J* 3 and 6 Hz) and 8.23 (dd, *J* 3 and 6 Hz), respectively, which result from protons in a *peri*-relationship with the benzeneselenenyl moiety.

The formation of the product (7) is believed to arise from compound (6) by further benzeneseleninylation at the 1-position, followed by deformylation. However, no experimental evidence was obtained to substantiate this proposal.

Oxidation of heterocyclic methylarenes was next investigated. 2-Methylpyridine, for example, with 0.33 mol equiv. of benzeneseleninic anhydride in chlorobenzene at 130 °C gave pyridine-2-carbaldehyde in 10% yield. A similar reaction with 2-methylquinoline gave quinoline-2-carbaldehyde in 59% yield, while 4-methylquinoline gave the corresponding aldehyde in 84% yield. Treatment of 4-methylquinoline with an excess of the anhydride (3 equiv.) over an extended period of time (22 h) gave, on work-up as the methyl ester, a 43% yield of quinoline-4-carboxylic acid methyl ester.

3-Methylisoquinoline, which contains a less activated methyl substituent, reacted slowly with the anhydride and only trace amounts of any carboxy-group containing product were observed. The main product which was isolated after chromatography was the selenenylisoquinoline (8) formed in 52% yield. Upon heating the isoquinoline for some 96 h in the presence of 1 equiv. of the anhydride an additional product was isolated in low yield (5%) and shown to be the diselenated derivative (9).

Not surprisingly, attempted oxidation of 3-methylpyridine was unsuccessful owing to the fact that the methyl group here is not activated by the heterocyclic ring. The reactivity pattern in the above examples parallels similar oxidation reactions using SeO<sub>2</sub>. However, the products in these reactions are usually acids.<sup>1a,7</sup> The use of benzeneseleninic anhydride as an alternative oxidant to selenium dioxide is additionally attractive in that the work-up is often much cleaner and free from troublesome deposits of colloidal selenium common to the SeO<sub>2</sub> oxidations.

Finally, it was of interest to study the oxidation of other alkyl substituted arenes by the anhydride. Diphenylmethane reacted only slowly in chlorobenzene at 90 °C. However, when treated neat using an excess of diphenylmethane at 59% yield of benzophenone could be isolated after 5 d. At higher temperatures in chlorobenzene (120 °C) for 4 d up to a 93% yield of benzophenone could be achieved.

Oxidation of ethylbenzene proceeded best when an excess of neat substrate was used. The products of the reaction were acetophenone, phenylglyoxal, and small amounts of a selenated product shown to be, by comparison with an authentic sample, compound (10).

In summary, therefore, it has been shown that benzene seleninic anhydride can be used as an oxidant for a number of benzylic hydrocarbons. The yields are comparable with similar reactions using selenium dioxide and the work-up conditions are more convenient.

#### EXPERIMENTAL

Melting points were determined using a Kofler hot stage apparatus and are uncorrected. I.r. spectra were recorded (in Nujol unless otherwise stated) on a Perkin-Elmer 298 spectrometer; n.m.r. spectra were recorded using a Varian EM 360 A machine for solutions in  $\text{CDCl}_3$ , using  $\text{Me}_4\text{Si}$  as internal standard. Mass spectra were recorded on A.E.I. MS9 or VG Micromass 7070 instruments. All solvents and reagents were purified by standard methods. Benzene-seleninic anhydride (BSA) was prepared by previously described methods.<sup>3</sup> For convenience, in small scale work aldehydes were isolated as their corresponding 2,4-dinitrophenylhydrazones (2,4-DNPH).

**Oxidation of Toluene with BSA.**—To an excess of toluene (2 ml) in a Carius tube was added BSA (120 mg, 0.33 mmol). The tube and contents were then heated at 120 °C for 1 week. The cold tube was opened and the deep yellow solution sampled by t.l.c., which showed the presence of benzaldehyde, benzoic acid, diphenyl diselenide, and traces of other products. A warm solution of 2,4-DNPH (250 mg) in methanol (5 ml), which contained concentrated sulphuric acid (0.5 ml), was added to give a yellow solid which was filtered and washed (aqueous MeOH) to give benzaldehyde-2,4-DNP (53 mg, 0.19 mmol), m.p. 238–241 °C (lit.,<sup>8</sup> m.p. 237 °C).

**Oxidation of *o*-Xylene with BSA.**—(a) To *o*-xylene (1.2 ml) was added BSA (120 mg, 0.33 mmol) and the stirred mixture was heated at 120 °C (oil-bath) for 17 h. Preparative layer chromatography (p.l.c.) ( $\text{CHCl}_3$ ) under  $\text{CO}_2$  then gave diphenyl diselenide (98 mg, 95%), m.p. 61–63 °C (lit.,<sup>9</sup> m.p. 63 °C); *o*-tolualdehyde (24 mg, 0.2 mmol) as its 2,4-DNP, m.p. 191–195 °C (lit.,<sup>10</sup> m.p. 193–194 °C); and *o*-toluic acid (22 mg, 0.16 mmol), m.p. 95–100 °C (lit.,<sup>11</sup> m.p. 102 °C).

(b) A stirred mixture of *o*-xylene (10 ml) and BSA (1 g) well flushed with nitrogen was heated to 120 °C for 20 h. (i) To a portion (1.005 g) of the resulting yellow solution (at room temperature) was added a warm solution of 2,4-DNPH (100 mg) in methanol (1 ml), which contained concentrated sulphuric acid (0.1 ml), to give an orange solid which was filtered, washed, and dried to give *o*-tolualdehyde-2,4-DNP (60 mg, 0.21 mmol); (ii) a portion (0.64 g), on p.l.c. ( $\text{CHCl}_3$ ) under carbon dioxide, gave diphenyl diselenide (64 mg, 95%), *o*-tolualdehyde (20 mg, 0.167 mmol), and *o*-toluic acid (8 mg, 0.06 mmol).

**Oxidation of Benzaldehyde with BSA.**—Pure benzaldehyde (600 mg, 5.7 mmol) and BSA (500 mg, 1.39 mmol) were heated at 120 °C for 5 h; t.l.c. showed the ready formation of benzoic acid and diphenyl diselenide. The deep orange solution (at room temperature) was rapidly shaken with diethyl ether and filtered off from the white crystalline benzeneseleninic acid (64 mg, 12%), m.p. 115–120 °C, (lit.,<sup>12</sup> m.p. 122–124 °C). The yellow ethereal filtrate was extracted with saturated sodium hydrogencarbonate (4 × 10 ml) and the aqueous extracts were acidified (sulphuric acid) to give a white crystalline solid which was filtered, washed (cold water), and air dried to give benzoic acid (300 mg, 2.46 mmol), m.p. 120 °C (lit.,<sup>13</sup> m.p. 121.4 °C). The

residual ether layer was dried ( $\text{Na}_2\text{SO}_4$ ), evaporated, and the residue subjected to p.l.c. (light petroleum) to give diphenyl diselenide (368 mg, 85%).

**Oxidation of *p*-Xylene with BSA.**—*p*-Xylene (10.5 ml) and BSA (0.95 g) were heated at 120 °C for 119 h. (i) To a portion (1.26 g) of the cold yellow solution was added a solution of 2,4-DNPH (80 mg) in methanol (1 ml), which contained concentrated sulphuric acid (0.05 ml), to give an orange solid which was filtered, washed, and dried to give *p*-tolualdehyde-2,4-DNP (108 mg, 0.36 mmol), m.p. 238–240 °C (lit.,<sup>14</sup> m.p. 232.5–234.5 °C); (ii) a portion (0.46 g) of the solution was subjected to p.l.c. ( $\text{CHCl}_3$ ) under carbon dioxide to give diphenyl diselenide (42 mg, 97%), m.p. 61–62 °C; *p*-tolualdehyde (18 mg, 0.15 mmol) as its 2,4-DNP, m.p. 237–239 °C (lit.,<sup>14</sup> m.p. 232.5–234.5 °C); *p*-toluic acid (6 mg, 0.044 mmol), m.p. 174–179 °C (lit.,<sup>15</sup> m.p. 177–178 °C), and traces of other products.

**Oxidation of 4-Methoxytoluene with BSA.**—(a) 4-Methoxytoluene (122 mg, 1 mmol) in a Carius tube with BSA (720 mg, 2 mmol) was heated at 120 °C for 2–4 h. The cold tube was opened (considerable internal pressure observed), the yellow crystalline mass was digested with dichloromethane, and filtered to give off-white crystals of benzeneseleninic acid (505 mg, 2.67 mmol, 67%), identical to authentic material. The yellow filtrate was subjected to p.l.c. (first elution, light petroleum; second elution, light petroleum–10%  $\text{Et}_2\text{O}$ ) to give diphenyl diselenide (64 mg, 0.205 mmol, 10%), 4-methoxybenzaldehyde (12 mg, 0.09 mmol, 9%) as its 2,4-DNP, m.p. 243–248 °C (lit.,<sup>16</sup> m.p. 248–250 °C), traces (<5%) of, presumably, 4-methoxybenzoic acid [see (b) below], and a mixture (129 mg) of unchanged starting material and compound (1) (*vide infra*), estimated by n.m.r. to contain starting material (20 mg, 0.16 mmol, 16%), the resubjection of which to p.l.c. (light petroleum, four elutions) gave 1-methoxy-4-methyl-2-phenylselenobenzene (1) (108 mg, 0.4 mmol, 40%) as a pale yellow oil;  $\nu(\text{CCl}_4)$  3 040 (w), 1 585 (w), 1 490 (vs), 1 475 (s), 1 460 (s), 1 435 (s), 1 290 (m), 1 270 (m), 1 235 (vs), 1 060 (s), 1 025 (m doublet), and 695  $\text{cm}^{-1}$  (s);  $\delta(\text{CCl}_4)$  7.6–6.9 (5 H, m, PhSe), 6.8 (dd,  $J$  2, 8 Hz), 6.65br (s), and 6.55 (d,  $J$  8 Hz) (the last three integrating for 3 H), 3.75 (3 H, s), and 2.1 (3 H, s);  $m/e$  278 ( $M^+$ ), 263, 248, 235, 198, 183, 168, 165, and 155;  $m^*$  141 and 169. (Found: C, 60.6; H, 5.05.  $\text{C}_{14}\text{H}_{14}\text{OSe}$  requires C, 60.66; H, 5.09%).

(b) The above experiment was repeated, but using BSA (180 mg, 0.5 mmol, 0.5 mol equiv.) and heating at 120 °C for 26.4 h. P.l.c. (light petroleum–10%  $\text{Et}_2\text{O}$ ) under carbon dioxide, as before, gave diphenyl diselenide, a trace of benzeneseleninic acid, and, as the main products, the selenide (1) (70 mg, 0.25 mmol, 25%) and 4-methoxybenzaldehyde (9 mg, 0.07 mmol, 7%), both identical with previous samples, and 4-methoxybenzoic acid (38 mg, 0.25 mmol, 25%), m.p. (from  $\text{H}_2\text{O}$ ) 180–183 °C (lit.,<sup>17</sup> m.p. 184 °C);  $\nu_{\text{max}}$  ( $\text{CHCl}_3$ ) 3 490–2 200  $\text{cm}^{-1}$ .

**Oxidation of 9,10-Dimethylantracene with BSA.**—(a) To 9,10-dimethylantracene (40 mg) in chlorobenzene (1 ml) was added BSA (140 mg, 2 mol equiv.) and the stirred mixture was heated at 110 °C under nitrogen for 35 min. The cold reaction mixture was filtered off from crystals of benzeneseleninic acid (55 mg, 37%) (identical with authentic material). The filtrate was evaporated to dryness (under reduced pressure), the residue dissolved in a little dichloromethane, and then subjected to p.l.c. [light petroleum (b.p. 60–80 °C)–50%  $\text{CH}_2\text{Cl}_2$ , double elution] under carbon dioxide to give (i) diphenyl diselenide, (ii) 9-formyl-10-

methylanthracene (24 mg, 56%) as yellow-orange crystals m.p. 169–171 °C (lit.,<sup>18</sup> m.p. 170–172 °C);  $\nu(\text{CCl}_4)$  2 860 (w), 2 760 (w), and 1 680  $\text{cm}^{-1}$  (vs);  $\delta(\text{CDCl}_3)$  11.5 (1 H, s), 9.02 (2 H, dd,  $J$  2, 4.5 Hz), 8.48 (2 H, dd,  $J$  2, 5 Hz), 7.8–7.45 (4 H, m), and 3.18 (3 H, s);  $m/e$  220 ( $M^+$ ) 205, 192, 191, and 165;  $m^*$  191 and 167.6; (iii) 9,10-diformylanthracene (8 mg, 18%) as deep orange crystals, m.p. 240–243 °C (lit.,<sup>19</sup> m.p. 241–244 °C);  $\nu(\text{CHCl}_3)$  2 820 (w), 1 720 (w), and 1 685  $\text{cm}^{-1}$  (vs) [lit.,<sup>19</sup>  $\nu(\text{KBr})$  1 680  $\text{cm}^{-1}$ ];  $m/e$  234 ( $M^+$ ), 206, 205, 178, 177, and 176;  $m^*$  181.4, 179.6, and 153.8.

(b) To 9,10-dimethylanthracene (20 mg) in chlorobenzene (0.5 ml) was added BSA (70 mg, 2 mol equiv.) and the mixture was heated at 120 °C under nitrogen for 20.5 h. The solvent was removed under reduced pressure and p.l.c. [light petroleum (b.p. 60–80 °C)–50%  $\text{CH}_2\text{Cl}_2$ , double elution] gave diphenyl diselenide (58 mg, 96%), m.p. 61–63 °C, and a band of material which was resubjected to p.l.c. to give anthraquinone (13 mg from  $\text{CCl}_4$ ; 64%) as slightly discoloured crystals, m.p. 284–287 °C (lit.,<sup>20</sup> m.p. 285–286 °C);  $\nu_{\text{max.}}$  ( $\text{CHCl}_3$ ) 1 680  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$  8.3 (4 H, dd,  $J$  3, 6 Hz) and 7.75 (4 H, dd,  $J$  3, 6 Hz);  $m/e$  208 ( $M^+$ ), and identical in all respects with authentic material.

*Reaction of 1,3-Dimethoxy-2-methylbenzene with BSA.*—(a) To 1,3-dimethoxy-2-methylbenzene (76 mg, 0.5 mmol) in chlorobenzene (0.5 ml) was added BSA (60 mg, 0.167 mmol, 0.33 mol equiv.) and the mixture was heated at 110 °C under nitrogen for 17 h. The cold mixture was filtered off from a little benzeneseleninic acid (identical with authentic material) and the filtrate was passed down a short column (silica gel MFC, 100 mesh) with light petroleum as eluant to remove chlorobenzene, then with light petroleum–10% diethyl ether to obtain the reaction products which were subjected to p.l.c. (light petroleum–10%  $\text{Et}_2\text{O}$ ) to yield unchanged starting material (10 mg, 13%) and 1,3-dimethoxy-2-methyl-4-phenylselenobenzene (2) (75 mg, 49%) as a pale yellow oil;  $\nu(\text{neat})$  3 060(w), 3 050 (w), 3 000–2 800 (m), 1 775 (m), 1 465 (s), 1 440 (m), 1 395 (m), 1 290 (m), 1 270 (s), 1 225 (m), 1 110 (vs), 1 025 (m), 1 005 (m), 805 (m), 740 (m), and 695 (m)  $\text{cm}^{-1}$ ;  $\delta(\text{CCl}_4)$  7.45–7.05 (5 H, m, PhSe), 6.94 and 6.38 (1 H + 1 H, ABq,  $J$  8.5 Hz), 4.73 (3 H, s), 3.70 (3 H, s), and 2.13 (3 H, s);  $m/e$  308 ( $M^+$ ) and 228 (Found: C, 58.4; H, 5.5.  $\text{C}_{15}\text{H}_{16}\text{O}_2\text{Se}$  requires C, 58.64; H, 5.25%).

(b) To 1,3-dimethoxy-2-methylbenzene (76 mg) in chlorobenzene (0.5 ml) was added BSA (180 mg, 1 mol equiv.) and the mixture was heated at 110 °C for 17 h. Work-up as in (a) gave benzeneseleninic acid (72 mg, 38%) and a mixture of reaction products which was subjected to p.l.c. (light petroleum–10%  $\text{Et}_2\text{O}$ ) to give a little diphenyl diselenide, the selenide (2) (131 mg, 85%), identical to the previous sample, and 2,4-dimethoxy-3-methyl-1,5-diphenylselenobenzene (3) (11 mg, 5%) as a pale orange solid;  $\nu(\text{CCl}_4)$  3 050 (w), 3 000–2 750 (m), 1 575 (w), 1 480 (m), 1 455 (s), 1 440 (s), 1 245 (m), 1 215 (m), 1 170 (m), 1 095 (s), 1 025 (m), 1 010 (m), and 700  $\text{cm}^{-1}$  (s);  $\nu(\text{CS}_2)$  750 (vs) and 700  $\text{cm}^{-1}$  (s), *inter alia*;  $\delta(\text{CCl}_4)$  7.45–6.95 (10 H, m), 6.40 (1 H, s), 3.75 (6 H, s), and 2.22 (3 H, s);  $m/e$  464 ( $M^+$ ), 499, 421, 368, 353, 292, and 212, accurate  $M^+$  at  $m/e$  463.9790 (<sup>80</sup>Se peak) (Calculated for  $\text{C}_{21}\text{H}_{20}\text{O}_2\text{Se}$ , 463.9792).

*Reaction of 1,3-Dimethoxy-2-methylbenzene with Benzeneselenenic Anhydride (PhSeOSePh; from Comproportionation<sup>5</sup> of DPDS and BSA).*—To diphenyl diselenide (DPDS) (416 mg, 1.33 mmol, 0.67 mol equiv.) in chlorobenzene (2 ml) was added BSA (240 mg, 0.67 mmol, 0.33 mol equiv.), and the mixture was stirred for 10 min. Then 1,3-dimethoxy-2-

methylbenzene (304 mg, 2 mmol) was added and the mixture was heated at 120 °C under nitrogen for 16 h. Most of the solvent was removed from the resulting yellow solution and the residue was taken up in chloroform, which contained a little methanol, and subjected to p.l.c. (first elution, light petroleum–5%  $\text{Et}_2\text{O}$ ; second elution, light petroleum to give diphenyl diselenide (235 mg, 38% based on DPDS + BSA), the selenide (2) (560 mg, 91%), and the bis-selenide (3) (7 mg, 0.8%), all identical with previous or authentic materials.

*Reaction of 1,3-Dimethoxy-2-methylbenzene with Benzeneselenenyl Chloride.*—To 1,3-dimethoxy-2-methylbenzene (206 mg, 1.33 mmol) in dry benzene (1 ml) was added a solution of benzeneselenenyl chloride (255 mg, 1.33 mmol) in benzene (1 ml), and the stirred mixture was heated to reflux for 21.5 h. P.l.c. gave diphenyl diselenide, starting material, and the selenide (2). The actual yield of compound (2) was estimated by n.m.r. spectroscopy to be 35 mg (9%).

*Preparation of 1,3-Dimethoxy-2-methyl-4-phenylseleninylbenzene (4).*—To the selenide (2) (102 mg, 0.33 mmol) in tetrahydrofuran (THF) (1 ml) was added 30% hydrogen peroxide (0.4 ml, *ca.* 10 equiv.) and the mixture was stirred at room temperature for 24 h. The solvent was removed (under reduced pressure), the residue was taken up in dichloromethane (20 ml) and washed thoroughly with saturated brine ( $2 \times 25$  ml), then water ( $4 \times 5$  ml), and then dried ( $\text{Na}_2\text{SO}_4$ ), evaporated (reduced pressure), and placed under high vacuum (overnight) to give the selenoxide (4) (92 mg, 85%) as a syrup (homogeneous on t.l.c.);  $\nu(\text{neat})$  3 040 (w), 1 585 (m), 1 570 (m), 1 460 (m), 1 440 (m), 1 265 (s), 1 215 (m), 1 100 (s), 995 (m), 830 (s, Se=O);  $\delta(\text{CCl}_4)$  7.77–7.47 (m) and 7.4–7.1 (m) (both together, 6 H), 6.7 (1 H, d,  $J$  8.5 Hz), 3.08 (3 H, s), 3.7 (3 H, s), and 2.07 (3 H, s).

*Deoxygenation of the Selenoxide (4).*—(a) *No additive.* A stirred solution of compound (4) (30 mg) in chlorobenzene (1 ml) was heated at 130 °C for a total of 18.5 h. The reaction was monitored by t.l.c. which showed the progressive formation of the selenide (3). The solvent was removed, and the residue taken up in dichloromethane and subjected to p.l.c. ( $\text{CHCl}_3$ ) which gave the selenide (3) (14 mg, 49%) and unchanged selenoxide (4) (12 mg, 40%), both identical with previous samples.

(b) *With diphenyl diselenide (1 mol equiv.).* To the selenoxide (4) (15 mg) in chlorobenzene (1 ml) was added diphenyl diselenide (15 mg, 1 mol equiv.) and the mixture was heated at 130 °C for 8 h. The final mixture was evaporated to dryness (under reduced pressure), the residue was digested with a little dichloromethane, and filtered to give white crystals of benzeneseleninic acid (2 mg, 11%), m.p. 110–115 °C. yellow filtrate was subjected to p.l.c. ( $\text{CHCl}_3$ ) to give diphenyl diselenide and the selenide (2) (15 mg, 100%), identical to previous samples.

*Oxidation of 1-Methylnaphthalene with BSA.*—(a) 1-Methylnaphthalene (142 mg, 1 mmol) in a Carius tube and BSA (360 mg, 1 mmol) were heated at 120 °C for 11.75 h. The cold tube was opened, the contents dissolved in a little dichloromethane and methanol, and the deep orange solution was subjected to p.l.c. [light petroleum (b.p. 60–80 °C)–10%  $\text{Et}_2\text{O}$ , triple elution] under carbon dioxide to give, in order of increasing polarity, (i) a yellow band (A) which was resubjected to p.l.c. (*vide infra*), (ii) 1-naphthaldehyde (9 mg, 6%);  $\nu(\text{CCl}_4)$  3 040 (w), 2 820 (w), 2 700 (w), and 1 700  $\text{cm}^{-1}$  (vs);  $\delta(\text{CCl}_4)$  10.25 (1 H, s), 9.2 (1 H, dd,  $J$  2.5, 6.5 Hz), and 8.1–7.3 (6 H, m), identical with authentic material, and

(iii) 4-phenylseleno-1-naphthaldehyde (6) (19 mg, 6%) as a yellow oil,  $\nu(\text{CCl}_4)$  3 040 (w), 2 820 (w), 2 700 (w), and 1 700  $\text{cm}^{-1}$  (vs);  $\delta$  (100 MHz,  $\text{CDCl}_3$ ) 10.29 (1 H, s), 9.31 (1 H, m), 8.28 (1 H, m), and 7.8—7.2 (9 H, m);  $m/e$  312 ( $M^+$ ), 283, 282, 232, 231, 204, and 203;  $m^*$  257.5; 178.4, and 172.5; obtained as its 2,4-dinitrophenylhydrazone as orange crystals (from pyridine-methanol), m.p. 226—231 °C (Found: C, 56.45; H, 3.35; N, 11.6.  $\text{C}_{23}\text{H}_{16}\text{O}_4\text{N}_4\text{Se}$  requires C, 56.22, H, 3.28; N, 11.40%). There were also small quantities of other polar products which were not investigated further. The material in the yellow band (A) (*vide supra*) was subjected to p.l.c. (light petroleum, triple elution) to give, in order of increasing polarity, (i) traces of starting material, (ii) diphenyl diselenide (228 mg, 73%), m.p. 61—63 °C, (iii) 1-methyl-4-phenylselenonaphthalene (5) (57 mg, 19%) as a pale yellow, low-melting solid;  $\nu$  (neat) 3 040 (w), 1 580 (m), 1 475 (m), 1 435 (m), 1 375 (m), 1 020 (m), 830 (m), 760 (s), 740 (s), and 695  $\text{cm}^{-1}$  (m);  $\delta(\text{CCl}_4)$  8.30 (1 H, dd,  $J$  3.5, 6.5 Hz), 7.88 (1 H, dd,  $J$  3.5, 6.5 Hz), 7.8—7.25 (4 H, m), 7.25—6.9 (5 H, m), and 2.65 (3 H, s);  $m/e$  298 ( $M^+$ ), 218, 203, 202, 141, and 115;  $m^*$  189 and 159.5, and identical to an authentic sample prepared by an independent route. The picrate was prepared (scarlet-vermilion needles from ethanol), m.p. 94—95 °C (Found: C, 52.35; H, 3.2; N, 7.9.  $\text{C}_{23}\text{H}_{17}\text{O}_7\text{N}_3\text{Se}$  requires C, 52.48; H, 3.26; N, 7.98%), and (iv) 1,4-diphenylselenonaphthalene (7) (25 mg, 6%) as needles [from light petroleum (b.p. 60—80 °C)], m.p. 130—131 °C;  $\nu(\text{CCl}_4)$  3 040 (w), 1 480 (s), 1 440 (m), 1 020 (m), 970 (m), and 700  $\text{cm}^{-1}$  (s);  $\nu(\text{CS}_2)$  3 040 (w), 1 030 (m), 975 (m), 835 (m), 770 (s), 750 (vs), 745 (vs), and 700  $\text{cm}^{-1}$  (s);  $\delta(\text{CCl}_4)$  8.25 (1 H, dd,  $J$  3.5, 6.5 Hz), 7.43 (s, 2- and 3-H) and 7.65—7.0 (m) (both together, 14 H);  $m/e$  440 ( $M^+$ ), 360, 283, and 202 (Found: C, 60.4; H, 3.65.  $\text{C}_{22}\text{H}_{16}\text{Se}_2$  requires C, 60.29; H, 3.68%).

(b) To 1-methylnaphthalene (284 mg, 2 mmol) was added BSA (180 mg, 0.5 mmol) and the mixture heated at 120 °C for 14 h. Direct p.l.c. (light petroleum-10%  $\text{Et}_2\text{O}$ ) under carbon dioxide gave two main product bands, an upper yellow band (A) and a lower band (B), as well as small quantities of many other polar materials. P.l.c. (light petroleum, triple elution) of the material in the upper band (A) gave unchanged starting material (210 mg, 74%), diphenyl diselenide (125 mg, 80%), and the contaminated selenide (5) (72 mg crude, 46%) which, on replating (light petroleum) gave the pure selenide (5) (50 mg, 8%), all identical with previous or authentic materials. P.l.c. (light petroleum-10%  $\text{Et}_2\text{O}$ , double elution) under carbon dioxide of the material from band (B) gave 1-naphthaldehyde (30 mg, 37%) and the aldehyde-selenide (6) (3 mg, 2%), all identical with previous samples. Yields are based on starting material consumed.

*Preparation of the Selenide (5).*—To the Grignard reagent formed from 4-bromo-1-methylnaphthalene (2.21 g) in dry diethyl ether (25 ml)-benzene (10 ml) and magnesium (0.25 g) was slowly added (reaction mixture heated to reflux) a solution of benzeneselenenyl chloride (in dry benzene), maintaining boiling, until the deep red colour of the selenium reagent just persisted. The mixture was heated for a further 15 min and the resultant mixture was diluted with diethyl ether (to 100 ml), water (20 ml) was added, and the mixture was shaken well. The organic layer was washed with water (5 × 15 ml), dried ( $\text{Na}_2\text{SO}_4$ ), and evaporated to give a brown oil which was subjected to p.l.c. (light petroleum, triple elution) to give the naphthalene (5) (0.61 g), identical in all respects with the earlier samples.

*Oxidation of 2-Methylpyridine with BSA.*—To 2-methylpyridine (93 mg, 1 mmol) in chlorobenzene (1 ml) was added BSA (120 mg, 0.33 mmol) and the mixture was heated at 130 °C for 3 h. To the warm deep yellow reaction mixture was added a solution of 2,4-DNPH (200 mg) in methanol (2 ml) that contained concentrated sulphuric acid (0.2 ml). A yellow solid was obtained which was filtered, washed, dried, and recrystallized from pyridine-methanol to give pyridine-2-carbaldehyde-2,4-DNP, m.p. 232—235 °C (lit.,<sup>21</sup> m.p. 235 °C).

*Oxidation of 4-Methylquinoline with BSA.*—(a) To 4-methylquinoline (71.5 mg, 0.5 mmol) in chlorobenzene (0.5 ml) was added BSA (180 mg, 0.5 mmol) and the mixture was heated at 130 °C for 17 min. Direct p.l.c. ( $\text{CHCl}_3$ ) under carbon dioxide gave diphenyl diselenide, benzeneseleninic acid, and quinoline-4-carbaldehyde (63 mg, 80%), m.p. 48—50 °C (lit.,<sup>22</sup> m.p. 48—49 °C);  $\nu(\text{CCl}_4)$  2 830 (w), 2 730 (w), and 1 710  $\text{cm}^{-1}$  (vs);  $\delta(\text{CCl}_4)$  10.35 (1 H, s), 9.05—8.75 (2 H, m), 8.2—7.9 (1 H, m), and 7.8—7.45 (3 H, m) the *p*-nitrophenylhydrazone derivative was obtained yellow needles (from ethanol-acetic acid), m.p. 262—264 °C (lit.,<sup>23</sup> m.p. 261—262 °C).

(b) To 4-methylquinoline (48 mg, 0.33 mmol) in dichlorobenzene (1 ml) was added BSA (360 mg, 1 mmol) and the mixture was heated at 130 °C for 22 h. The cold mixture was shaken with diethyl ether (2 ml) and filtered to leave a residue and an ether layer (A). The residue was shaken with sodium metabisulphite solution and diethyl ether (5 ml). A pellet of sodium hydroxide was added and the mixture shaken further. The layers were separated to give an ether layer (B) and an aqueous layer which was acidified and evaporated to dryness (under reduced pressure) to give a white solid to which was added an ethereal solution of diazomethane. After 1 h the excess of diazomethane was destroyed with acetic acid. The mixture was then filtered through anhydrous sodium sulphate and evaporated to give quinoline-4-carboxylic acid methyl ester (25 mg, 43%) as a low-melting solid, m.p. (from MeOH) 21—24 °C (lit.,<sup>24</sup> m.p. 24 °C);  $\nu(\text{CCl}_4)$  3 070 (w), 3 030 (w), 1 732 (vs), and 1 275  $\text{cm}^{-1}$  (vs). From the ether layer (A) (*vide supra*) was recovered diphenyl diselenide (105 mg, 33%), and from the layer (B) was recovered the same compound (140 mg, 45%), formed from residual benzeneseleninic acid from the reaction mixture.

*Oxidation of 3-Methylisoquinoline with BSA.*—(a) To 3-methylisoquinoline (71 mg, 0.5 mmol) in chlorobenzene (0.5 ml) was added BSA (180 mg, 0.5 mmol, 1 mol equiv.) and the mixture was heated at 120 °C for 48 h. The mixture was diluted with dichloromethane, filtered from benzeneseleninic acid (75 mg, 40%), m.p. 110—118 °C, and the filtrate was concentrated and subjected to p.l.c. (first elution, light petroleum-10%  $\text{Et}_2\text{O}$ ; second elution, light petroleum-20%  $\text{Et}_2\text{O}$ ) to give (*inter alia*) diphenyl diselenide and the main product 3-methyl-4-phenylselenoisoquinoline (8) (77 mg, 52%) as a pale yellow oil;  $\nu(\text{CCl}_4)$  3 040 (w), 1 615 (m), 1 570 (m), 1 476 (s), 1 430 (m), 1 230 (m), 1 020 (m), and 695  $\text{cm}^{-1}$  (m);  $\delta(\text{CCl}_4)$  9.07 (1 H, s, 1-H), 8.33 (1 H, m, 5-H, *peri* to Se), 7.95—7.35 (3 H, m), 7.0 (5 H, s, PhSe), and 2.88 (3 H, s);  $m/e$  299 ( $M^+$ ), 284, 258, 219, and 218;  $m^*$  160.4, accurate  $M^+$  at  $m/e$  299.0209 (<sup>78</sup>Se peak) (Calculated for  $\text{C}_{16}\text{H}_{13}\text{N}_2\text{Se}$ , 299.0213).

(b) The above experiment was repeated with heating for 96 h. P.l.c. ( $\text{CHCl}_3$ ) on the resulting crude product gave (i) diphenyl diselenide, (ii) 3,4-diphenylselenoisoquinoline (9) (11 mg, 5%) as a light yellow oil;  $\nu(\text{CCl}_4)$  3 040 (w), 1 615 (m),

1 475 (s), 1 435 (m), 1 385 (s), 1 095 (m), 1 020 (m), 960 (m), and 695  $\text{cm}^{-1}$  (s);  $\delta(\text{CCl}_4)$  8.85 (1 H, s, 1-H), 8.20 (1 H, m, 5-H, *peri* to Se at C-4), and 7.9—7.0 (13 H, m); *m/e* 441 ( $M^+$  two Se), 364 (two Se;  $M^+ - \text{Ph}$ ), 284 (one Se;  $M^+ - \text{Ph} - \text{Se}$ ), 283 (one Se), and 204 (*m/e* 284 - Se);  $m^* \text{ ca. } 300$  and 221.6, (iii) the selenide (8) (37 mg), identical with previous samples, and (iv) a broad band near the base line that contained several components and which had  $\nu(\text{CCl}_4)$  3 040—2 000br, 1 775 (m), and 1 740  $\text{cm}^{-1}$  (s), which was resubjected to p.l.c. (light petroleum—20%  $\text{Et}_2\text{O}$ , double elution) to give, as the only characterizable nitrogen-containing product the selenide (8) (17 mg), identical to the previous sample. Total yield of compound (8), 54 mg, 36%.

**Oxidation of Diphenylmethane with BSA.**—(a) To diphenylmethane (680 mg, 4 mmol) was added BSA (90 mg, 0.25 mmol) and the mixture was heated at 90 °C for 5 d. The resulting mixture was diluted with methanol (0.5 ml) and subjected to p.l.c. ( $\text{CH}_2\text{Cl}_2$ ) to give diphenyl diselenide, unchanged starting material, and benzophenone (38 mg, 0.22 mmol), m.p. 46—48 °C (lit.,<sup>25</sup> 48—48.5 °C);  $\nu(\text{CCl}_4)$  1 670 (vs), 1 280 (vs), 940 (s), 920 (s), and 705  $\text{cm}^{-1}$  (s);  $\delta(\text{CCl}_4)$  7.75—7.05 (10 H, m).

(b) To diphenylmethane (84 mg, 0.5 mmol) in chlorobenzene (2 ml) was added BSA (90 mg, 0.25 mmol, 0.5 mol equiv.) and the mixture was heated at 120 °C for 4 d. Concentration (under reduced pressure) of the resulting mixture and p.l.c. ( $\text{CH}_2\text{Cl}_2$ ) gave diphenyl diselenide, unchanged starting material, and benzophenone (64 mg, 0.35 mmol, 70%; 93% if 0.67 mol equiv. of BSA is the theoretical amount required).

**Oxidation of Ethylbenzene with BSA.**—To an excess of ethylbenzene (200 mg) was added BSA (90 mg, 0.25 mmol) and the mixture was heated at 85 °C for 10 min. The cloudy yellow resulting mixture was diluted with a little methanol to give a clear yellow solution which was subjected to p.l.c. ( $\text{CH}_2\text{Cl}_2$ ) to give (i) some diphenyl diselenide and unchanged starting material, (ii)  $\alpha$ -benzeneselenenylacetophenone (10) (6 mg, 0.02 mmol) as a pale yellow oil;  $\lambda(\text{MeOH})$  248 ( $\epsilon$  14 500) and 346 nm (1 000);  $\nu(\text{CCl}_4)$  1 685 (s) and 1 265  $\text{cm}^{-1}$  (s); *m/e* 276 ( $M^+$ ), 119, 105, 91, and 77, and identical with a sample prepared below, (iii) acetophenone (27 mg, 0.225 mmol)  $\lambda(\text{CH}_2\text{Cl}_2)$  243 ( $\epsilon$  12 000), 280 (1 200), and 288sh nm ( $\epsilon$  900) [lit.,<sup>26</sup>  $\lambda(\text{EtOH})$  242 ( $\epsilon$  12 300) and 280 nm (1 050)], and identical with authentic material, and (iv) phenylglyoxal (10 mg, ca. 0.07 mmol) isolated as a partial hydrate,  $\nu(\text{CCl}_4)$  3 350—3 200br (w.), 1 700 (s), 1 280 (s), 1 110 (s), 1 085 (vs), 980 (s), and 700  $\text{cm}^{-1}$  (s), and its hydrate, m.p. (from  $\text{H}_2\text{O}$ ) 88—91 °C (lit.,<sup>27</sup> m.p. 91 °C), and its di-2,4-DNP as yellow-orange crystals, m.p. 291—295 °C (lit.,<sup>28</sup> 295—297 °C).

**Preparation of  $\alpha$ -Benzeneselenenylacetophenone (10).**—To benzeneselenenyl bromide (472 mg, 2 mmol) in dry carbon tetrachloride was added acetophenone (260 mg, 3 mmol) and the stirred mixture was heated to reflux for 6 h. The cold reaction mixture was evaporated (under reduced pressure) to dryness, the residue was digested with light petroleum, and filtered. The yellow filtrate was evaporated to leave an oil which was dissolved in light petroleum (2 ml) and subjected to column chromatography (silica gel MFC, 100 mesh). Elution with light petroleum (to give mainly diphenyl diselenide) followed by dichloromethane gave, as the main product, the title compound (10) (162 mg, 29%) as a light coloured oil;  $\lambda(\text{MeOH})$  248 ( $\epsilon$  14 200) and 346 nm (1 100);  $\nu(\text{CCl}_4)$  3 030 (w), 1 685 (vs), 1 600 (m), 1 450 (s), 1 310 (m),

1 300 (m), 1 270 (vs), 1 190 (m), 1 180 (m), 1 010 (m), 705 (m), and 690  $\text{cm}^{-1}$  (s);  $\delta(\text{CCl}_4)$  8.1—7.65 and 7.6—7.0 (10 H, m), and 4.33 (2 H, s); *m/e* 276 ( $M^+$ , one Se), 119, 105, 91, and 77. This ketone is a known compound.<sup>29</sup>

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