

## Deselenation and the Mass Spectra of 3,3'-Di-indolyl Selenides

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3,3'-Di-indolyl selenide and 3,3'-di(1-methyl-indolyl) selenide when treated with Raney nickel give bi-indolyls or indoles depending upon the nature of the catalyst. The mass spectral fragmentation and the photochemical decomposition of these compounds involve similar deselenations.

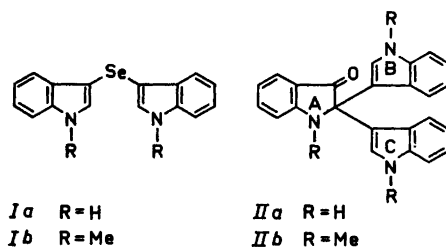
The reaction which takes place when indole is treated with selenium dioxide in benzene has been studied by Witkop<sup>1</sup> and Wilshire<sup>2</sup> and the latter has shown that the main product formed is 3,3'-di-indolyl selenide (Ia).

In the present investigation it has been shown that on treatment with degassed Raney nickel, 3,3'-di-indolyl selenide gives 3,3'-bi-indolyl in good yield. However using "Raney nickel W-6" only indole is obtained. In this connection it is of interest that pyrolysis of, *e.g.* diphenyl sulfide and diphenyl selenide give biphenyl derivatives; see Ref. 3.

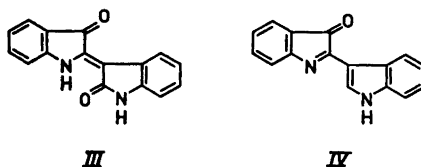
1-Methylindole on treatment with selenium dioxide gave 3,3'-di(1-methyl-indolyl) selenide (Ib) together with a trimeric substance for which structure IIb is suggested. The parent trimer (IIa) has been obtained by Witkop and Patrick<sup>4</sup> by oxidation of indole with hydrogen peroxide.

The structure of the selenide Ib follows from its composition and mass spectrum (Fig. 2). Deselenations gave 1,1'-dimethyl-3,3'-bi-indolyl (degassed Raney nickel) and 1-methylindole (W-6 Raney nickel).

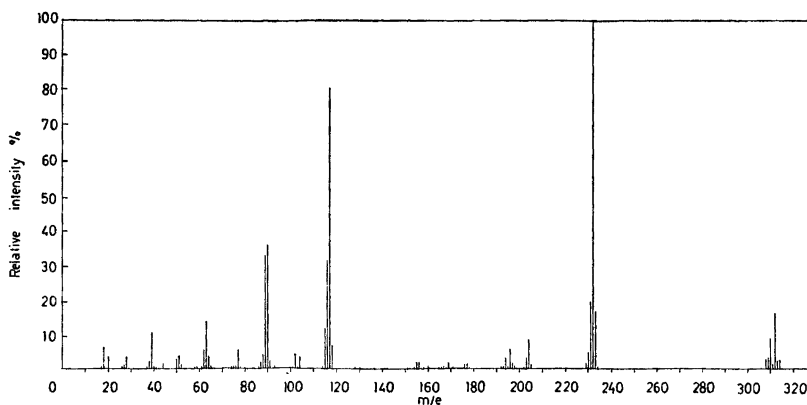
In accordance with the structure suggested, the NMR spectrum of compound IIb showed in addition to the fourteen aromatic protons, only peaks at  $\tau=3.5$  (6 H) corresponding to the methyl groups attached to the rings B and C and at  $\tau=3.2$  (3 H) corresponding to the methyl group attached to ring A. The IR-spectrum showed a strong carbonyl absorption at  $1725\text{ cm}^{-1}$  and the mass spectrum showed strong peaks (more than 10 % of the base peak) at  $m/e$ : 405 (100 %, parent ion), 406 (36 %), 376 (63 %, loss of methylene imine), 377 (26 %), 275 (19 %, loss of one 1-methylindolyl group), 247 (49 %), 202.5 (21 %).



Since 1-methylindole gave a selenium-free coupling product with selenium dioxide, it was of some interest to investigate also the by-products obtained from indole. A TLC analysis of the reaction products showed the presence of several substances. These were isolated by column chromatography and identified as 1) indole, 2) 3,3'-di-indolyl selenide, 3) 3,3'-di-indolyl diselenide, 4) *IIa*,<sup>4</sup> 5) indirubin (*III*),<sup>5</sup> 6) indoxyl red (*IV*).<sup>4</sup> No indigo was detected. The 3,3'-di-indolyl selenide was contaminated with small amounts of a triselenide and traces of a tetraselenide as shown by mass spectrometry but two recrystallizations gave a pure product identical with an authentic sample.<sup>6</sup>



The mass spectra of the selenides *Ia* (Fig. 1) and *Ib* (Fig. 2) show that the corresponding bi-indolyls are formed during fragmentation. Metastable ions appeared near 173 (*Ia*) and 200 (*Ib*). These facts indicate that these



*Fig. 1.* Mass spectrum of 3,3'-di-indolyl selenide.

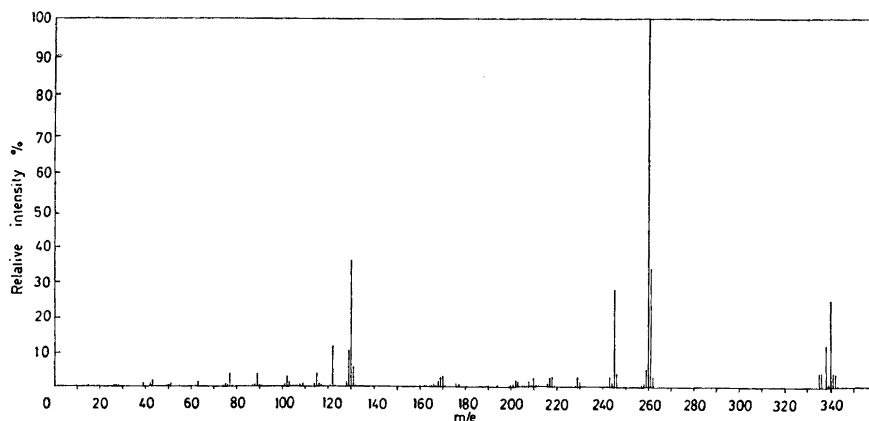
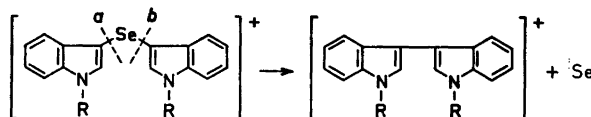


Fig. 2. Mass spectrum of 3,3'-di(1-methyl-indolyl) selenide.

selenides undergo simultaneous fission at the carbon-selenium-bonds (a and b), followed by recombination of the fragments as shown in Scheme I.



Scheme I

This type of fragmentation and recombination seems to be general for aryl selenides. In the mass spectrum of diphenyl selenide which shows  $(C_{12}H_{10})^+$  as the most abundant ion there are strong peaks (more than 10 % of base peak) at: 234  $(C_{12}H_{10}Se)^+$  44 %, 157  $(C_6H_5Se)^+$  49 %, 154  $(C_{12}H_{10})^+$  100 % after correction for  $(C_6H_5^{77}Se)^+$ , 78  $(C_6H_6)^+$  59 %, 77  $C_6H_5^+$  and  $(C_{12}H_{10})^{2+}$  98 %, 76  $(C_6H_4)^+$  22 %, 65  $(C_5H_5)^+$  14 %, 51  $(C_4H_3)^+$  68 %, 50  $(C_4H_4)^+$  16 %, 39  $(C_3H_3)^+$  22 %. (The intensities of ions containing isotopes of selenium other than  $^{80}Se$  are not given). Diphenyl sulfide,<sup>7,8</sup> diphenyl disulfide,<sup>8,9</sup> benzophenone,<sup>10</sup> and azobenzene<sup>10</sup> seem to undergo similar reactions although, judging from the intensities of the  $(C_{12}H_{10})^+$  ions, to a much lesser extent. The mass spectrum of diphenyl ether<sup>10</sup> does not show any  $(C_{12}H_{10})^+$  ion.

The intense peak at  $m/e$  117 in the mass spectrum of 3,3'-di-indolyl selenide (Fig. 1), corresponding to the fragment ion  $(C_8H_7N)^+$ , may be formed from the parent ion  $(C_{16}H_{12}N_2Se)^+$  by an intramolecular hydrogen transfer. This fragment ion seems not to appear in the mass spectrum of 3,3'-bi-indolyl (Fig. 3).

The peaks near  $m/e$  195 (Fig. 1) and 210 (Fig. 2) corresponding to the fragment ions  $(C_8H_6NSe)^+$  and  $(C_9H_8NSe)^+$  respectively, are of low intensity. Strong metastable peaks around  $m/e$  69 (Ia) and 81 (Ib) indicate that these ions easily lose selenium:

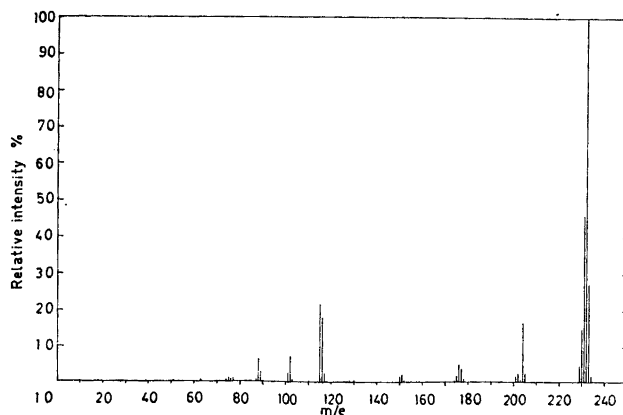


Fig. 3. Mass spectrum of bi-indolyl.



The corresponding diselenides which have been investigated independently by Agenäs<sup>11</sup> show a very similar fragmentation pattern.

3,3'-Bi-indolyl, indole, and selenium are also formed on ultraviolet irradiation (300 m $\mu$ , room temperature, benzene) of 3,3'-di-indolyl selenide (Ia).

### EXPERIMENTAL

Melting points were determined on a micro hot stage and are uncorrected. IR spectra: Perkin Elmer 237 spectrometer (KBr). NMR spectra: Varian A 60 spectrometer. UV: Beckman DK2. Mass spectra: LKB 9000 instrument at 120° (Compounds Ia and Ib), 25° (diphenyl selenide), 100° (3,3'-bi-indolyl) and 150° (compound IIb). Thin layer chromatograms were run with 99:1 chloroform-ethanol, on silica gel G (Merck) and sprayed with phosphomolybdic acid. All  $R_F$ -values given were determined by TLC.

*Reaction of 1-methylindole with selenium dioxide.* Finely ground selenium dioxide (Merck *p.a.*) (15 g) was added to a solution of 1-methylindole (10 g) in benzene (200 ml) and the mixture was heated on the steam bath for 0.5 h. The selenium formed was filtered off and light petroleum (60–70°, 400 ml) was added. The light-brown precipitate was washed with light petroleum and dried (3.1 g). The filtrate contained unreacted 1-methylindole. The precipitate was dissolved in methylene chloride and chromatographed on silica gel (100 g) using methylene chloride as eluent. This gave 3,3'-di(1-methyl-indolyl) selenide (Ib) (2.2 g;  $R_F=0.93$ ) and the trimeric compound IIb (0.8 g;  $R_F=0.78$ ).

Compound Ib was recrystallized from methylene chloride (cooling to –20°), m.p. 163–165°. (Found: C 63.7; H 4.6; N 8.0. Calc. for  $\text{C}_{15}\text{H}_{16}\text{N}_2\text{Se}$ : C 63.8; H 4.8; N 8.3).

Compound IIb was recrystallized from ethyl acetate, m.p. 214–216°. (Found: C 79.5; H 5.8, N 10.1. Calc. for  $\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}$ : C 80.0; H 5.7; N 10.4).

*Reaction of indole with selenium dioxide.* Indole (10 g) in benzene (200 ml) was treated in the same way with selenium dioxide (15 g). The filtrate was evaporated to 40 ml under reduced pressure and then chromatographed on silica gel (300 g), using light petroleum/benzene (1:1) taking 200 ml in each fraction. Fractions 1–23 contained indole

(4.6 g,  $R_F=0.84$ ). Fractions 34–49 contained 3,3'-di-indolyl selenide ( $R_F=0.53$ ) and 3,3'-di-indolyl diselenide ( $R_F=0.47$ ). Elution with methylene chloride (1.5 l), followed by methanol (1 l) gave a mixture (0.6 g) of trimerid IIa ( $R_F=0.16$ ), indirubin ( $R_F=0.07$ ) and indoxyl red ( $R_F=0.02$ ). These compounds were separated by preparative TLC (silica gel HF, 1.5 mm layer,  $\text{CH}_2\text{Cl}_2$ ), and gave IR-spectra identical with those of authentic samples. Fractions 44–45 rechromatographed on silica gel (100 g, benzene) gave crude 3,3'-di-indolyl diselenide<sup>6</sup> (0.12 g) which was recrystallized twice from methanol/water; m.p. and mixed m.p. 177–179°.

*3,3'-Di-indolyl selenide (Ia).* The reaction of indole with selenium dioxide was repeated and the evaporated solution (40 ml) was cooled to 10°. Two recrystallizations of the product from methanol gave pure, colourless material. (3.0 g, 22 %, m.p. 200–201°, Lit.<sup>2</sup> 196–198°).

*Photochemical decomposition of 3,3'-di-indolyl selenide.* 3,3'-Di-indolyl selenide (1.0 g) in benzene (200 ml) was illuminated (300 m $\mu$ ) in a photoreactor (Rayonet RPR 100) for 48 h at room temperature. The solution gradually turned ruby-red and Se began to crystallize out on the walls of the reaction vessel. Separation of the components of the reaction mixture by preparative TLC (silica gel HF) gave indole (0.12 g), 3,3'-bi-indolyl (0.33 g) and unchanged starting material (0.36 g). No spots corresponding to higher selenides or to 2,3'-bi-indolyl were detected.

*Reaction of 3,3'-di-indolyl selenide with Raney nickel.* a) 3,3'-Di-indolyl selenide (2.0 g) in dioxan (100 ml) was boiled under reflux with Raney nickel W-6 (10 g) for 2 h. The mixture was filtered and evaporated. The residue recrystallized from cyclohexane gave indole (0.6 g).

b) The same procedure as in a) was repeated on 10 times the scale using degassed<sup>12</sup> Raney nickel. The crude product on recrystallization from ethanol gave 3,3'-bi-indolyl (9.0 g, 59 %), m.p. 285–287°. (Lit.<sup>13</sup> 284–286°).

*Reaction of 3,3'-di(1-methyl-indolyl) selenide with Raney nickel.* a) The same procedure as a) above was used. Distillation of the filtered reaction mixture gave 1-methylindole (0.7 g).

b) The same procedure as b) above gave 1,1-dimethyl-3,3'-bi-indolyl (10.2 g, 64 %), m.p. 185–187°. (Lit.<sup>14</sup> 186–188°). UV (ethanol):  $\lambda_{\text{max}}$  237, 308 m $\mu$  (log  $\epsilon$  4.41, 3.75).

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