

SELENIUM ANALOGS OF NATURALLY OCCURRING PRODUCTS. II<sup>1</sup>.Léopold LAITEM<sup>+</sup>, Léon CHRISTIAENS<sup>\*</sup>, and André WELTEROrganic Chemistry Laboratory, University of Liege, 4000 LIEGE, BELGIUM

Selenium analogs of desmethoxyharmaline (II), harmine (III) and hexadehydro yohimbane (IV) have been synthesised.

Recently<sup>1</sup> we reported the synthesis of selenium analog of tryptamine I<sub>a</sub>. This molecule is an interesting starting material to perform synthesis of more elaborated selenium heterocycles.

Indeed, corresponding acetamine I<sub>b</sub> (m.p. 97°) is quantitatively obtained by reacting aqueous solution of crude I<sub>a</sub> hydrochloride with acetic anhydride. Its P.M.R. data (CDCl<sub>3</sub>, int. ref. HMDS<sup>x</sup>,  $\int$  ppm) are fully consistent with this structure (1,80, s, 3H, COCH<sub>3</sub>; 2,88, t, 2H, CH<sub>2</sub>, J = 6 Hz; 3,42, t, 2H, CH<sub>2</sub>N, J = 6 Hz; 5,88, s, 1H, NH; 7,55, s, 1H, H<sub>2</sub>; 6,98 - 7,81, m, 4H, H<sub>4-7</sub>).

Intramolecular cyclisation occurs when xylene solution of I<sub>b</sub> is heated with a slight excess of a mixture P<sub>2</sub>O<sub>5</sub>/POCl<sub>3</sub> (1 : 1). The new heterocyclic system II, isolated (94 %) as hydrochloride (m.p. 240°), has been characterised by P.M.R. [(D<sub>2</sub>O, int. ref. TMSPA<sup>xx</sup> Na,  $\int$  ppm) : 2,46, s, 3H, CH<sub>3</sub>; 2,82, t, 2H, CH<sub>2</sub>, J = 8,5 Hz; 3,72, t, 2H, CH<sub>2</sub>N, J = 8,5 Hz; 7,11 - 8,11, m, 4 ArH]. Aromatisation of II was carried on by 10 % palladium charcoal.

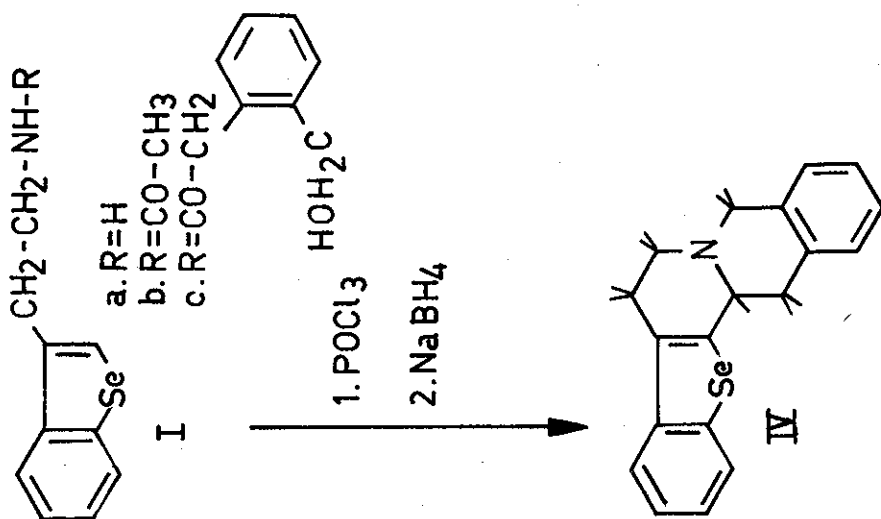
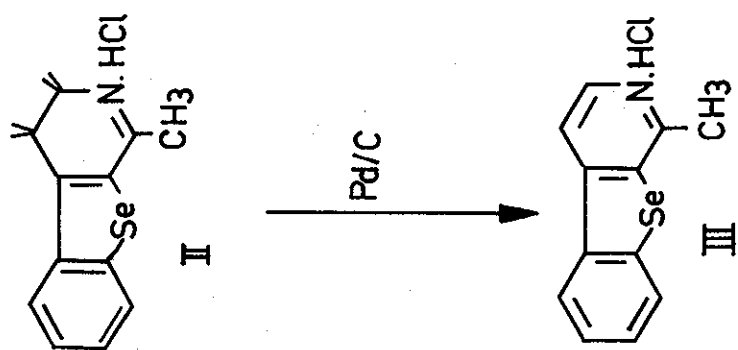
The harmine hydrochloride III thus obtained (58 %) presents the following P.M.R. data [(D<sub>2</sub>O, int. ref. TMSPA Na,  $\int$  ppm) : 2,39, s, 3H, CH<sub>3</sub>; 7,00 - 7,16, m, 6 ArH]. The corresponding (II and III) free bases were instable and could not be isolated.

On the other hand, condensation of crude selenotryptamine (I<sub>a</sub>) with 3-isochromanone<sup>2</sup> affords (72 %) the amide I<sub>c</sub> (m.p. 130°). Bischler-Napieralski intramolecular cyclisation, followed by sodium borohydride reduction, leads to the 1-seleno-15, 16, 17, 18, 19, 20-hexadehydroyohimbane (IV) (55 %, m.p. 193°).

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x Hexamethyldisiloxane

xx trimethylsilylpropionic acid sodium salt



The mass spectrum ( $^{80}\text{Se}$ ) confirms the molecular weight (339) and the presence of one selenium atom. This isolog of this new selenium ring system has been recently reported<sup>3</sup>. Complexity of the P.M.R. spectrum [(CDCl<sub>3</sub>, HMDS,  $\delta$  ppm) : 2,55 - 4,28, m, 9H; 7,00 - 8,00, m, 8H] prompts us to investigate the  $^{13}\text{C}$ .M.R. data. Those confirm (pyridine d<sub>5</sub>, int. ref. HMDS) the presence of five aliphatic carbons at 58,4 ppm, 56,4 ppm, 49,7 ppm, 37,4 ppm and 24,2 ppm.

All new compounds give satisfactory elemental analysis (C, H, N).

## REFERENCES

1. L. LAITEM and L. CHRISTIAENS, Bull. Soc. chim. France, 1975, 2294.
2. G.A. SWAN, J. Chem. Soc., 1949, 1720.
3. G. WOLF, W. MEISE and F. ZYMALKOWSKI, Tetrahedron Letters, 1972, 3223.

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