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SELENIUM ANALOGS OF NATURALLY OCCURRING PRODUCTS.II[1].

Léopold LAITEM[+], Léon CHRISTIAENS[*], and André WELTER
Organic Chemistry Laboratory, University of Liege, 4000 LIEGE, BELGIUM

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

Recently[1] we reported the synthesis of selenium analog of tryptamine I_a. This molecule is an interesting starting material to perform synthesis of more elaborated selenium heterocycles.

Indeed, corresponding acetamine I_b (m.p. 97°) is quantitatively obtained by reacting aqueous solution of crude I_a hydrochloride with acetic anhydride. Its P.M.R. data ($CDCl_3$, int. ref. HMDS[x], δ ppm) are fully consistent with this structure (1,80, s, 3H, $COCH_3$; 2,88, t, 2H, CH_2, J = 6 Hz; 3,42, t, 2H, CH_2N, J = 6 Hz; 5,88, s, 1H, NH; 7,55, s, 1H, H_2; 6,98 - 7,81, m, 4H, H_{4-7}).

Intramolecular cyclisation occurs when xylene solution of I_b is heated with a slight excess of a mixture $P_2O_5/POCl_3$ (1 : 1). The new heterocyclic system II, isolated (94 %) as hydrochloride (m.p. 240°), has been characterised by P.M.R. [(D_2O, int. ref. TMSPA[xx] Na, δ ppm) : 2,46, s, 3H, CH_3; 2,82, t, 2H, CH_2, J = 8,5 Hz; 3,72, t, 2H, CH_2N, J = 8,5 Hz; 7,11 - 8,11, m, 4 ArH]. Aromatisation of II was carried on by 10 % palladium charcoal.

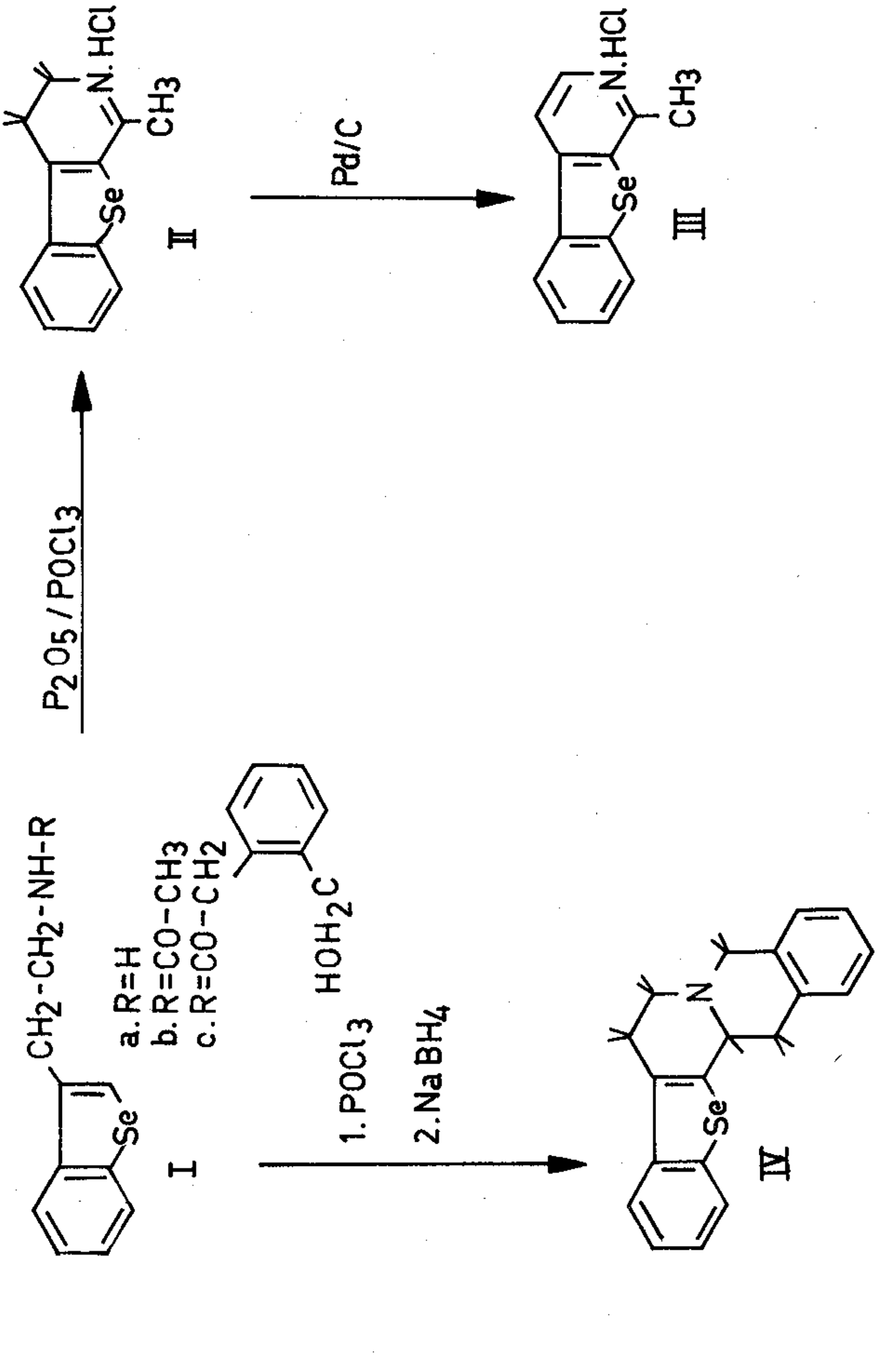
The harmine hydrochloride III thus obtained (58 %) presents the following P.M.R. data [(D_2O, int. ref. TMSPA Na, δ ppm) : 2,39, s, 3H, CH_3; 7,00 - 7,16, m, 6 ArH] . The corresponding (II and III) free bases were instable and could not be isolated.

On the other hand, condensation of crude selenotryptamine (I_a) with 3-isochromanone[2] affords (72 %) the amide I_c (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°).

[+] Aspirant of the "Fonds National de la Recherche Scientifique"

[x] Hexamethyldisiloxane

[xx] trimethylsilylpropionic acid sodium salt

CH2-CH2-NH-R
Se
I
a. R=H
b. R=CO-CH3
c. R=CO-CH2
HOH2C
P2O5 / POCl3
Se
N.HCl
CH3
II
Pd/C
Se
N.HCl
CH3
III
1. POCl3
2. NaBH4
Se
N
IV

The mass spectrum (^{80}Se) confirms the molecular weight (339) and the presence of one selenium atom. Thio isolog of this new selenium ring system has been recently reported[3]. Complexity of the P.M.R. spectrum $\left[(CDCl_3\right.$, HMDS, δ ppm) : 2,55 - 4,28, m, 9H; 7,00 - 8,00, m, 8H$\left.\right]$ prompts us to investigate the ^{13}C.M.R. data. Those confirm (pyridine d_5, 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).

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