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THE 1,3-BENZOTELLURAZOLE : A NEW HETEROCYCLIC SYSTEM

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Abstract : We describe the synthesis of a new heterocyclic system : the 1,3-benzotellurazole, and some of its substituted derivatives.

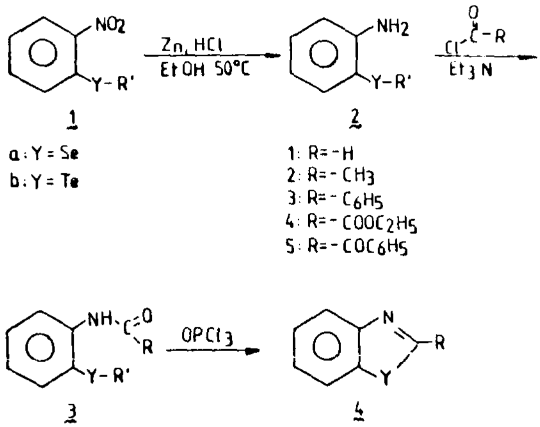
The chemistry of 1,3-benzoxazole[1], as well as of its sulfur[2] and selenium[3] analogs is well documented. Nevertheless, the 1,3-benzotellurazole (benzotellurazole), last term of this series is still unknown. During our work in progress on the comparative N.M.R. (^{1}H, ^{13}C, ^{77}Se and ^{125}Te) of chalcogenated heterocycles, we needed benzotellurazole and its derivatives.

An efficient strategy for their synthesis became available on one hand from a recent preparation of benzothiazoles[4] and on the other hand from our new easy elaboration of o-nitrotellurophenetole[5]. Indeed, as shown in scheme 1, o-nitroselenoanisole **1a** (R' = $-CH_3$)[6] and o-nitrotellurophenetole **1b** (R' = $-C_2H_5$) are cleanly reduced to the corresponding anilines **2**.

These anilines, after acylation by the appropriate acid chlorides or formylation by the formic acid-dicyclohexylcarbodiimide method [7], lead to the corresponding anilides **3** (most of them have not been isolated).

In our hands, among the lot of potential cyclising agents, phosphorous oxychloride was the more effective. Although the yields (not optimized) of benzochalcogenazoles are rather low (see table 1), our method affords rapidly and easily new benzoselenazoles (4a4 and 4a5) directly functionnalized in 2 position and the hitherto unknown benzotellurazoles. Work is at present in progress to explore the chemistry of this new heterocycle. Preliminary physico-chemical studies shows that the ^{13}C chemical shifts pattern in the 2-methyl benzochalcogenazoles shows a similar behaviour as that of phenylchalcogenolacetates[8].

So, we were able to establish a good linear correlation between the chemical shifts of $^{13}C_{-3a}$ in 4.1 and these of $^{13}C_{-2}$ in phenylchalcogenolacetates ($\delta_{C-3a} = 1.00\ \delta_{C-2} + 19{,}8\quad r = 0{,}98$).



scheme 1.

Typical experiment

Anilines 2a (R' = - CH_3) or 2b (R' = - C_2H_5) (2.10^{-2} mole) are dissolved in 20 ml of dichloromethane containing 5 ml of triethylamine. The mixture is cooled and 2,5 10^{-2} mole of the appropriate acid chloride in 10 ml of the same solvent is added dropwise at 0°C. The reaction mixture is stirred for 2 hours and after the usual work-up, the crude anilides are directly cyclised by refluxing 3 hours in 20 ml of phosphoroxychloride (compounds 3a2 (R' = - CH_3) and 3b2 (R' = - C_2H_5 were isolated).

After hydrolysis in the cold, the basic mixture is extracted with methylenechloride. The solution is dried, filtered and concentrated in vacuo. The residue is purified by distillation or chromatography on silicagel (eluent : hexane) followed by recristallization in the same solvent.

Table 1 (a)

Compound	Mp °C Bp °C/mm Hg	Yield[(b)] %	^1H N.M.R (d)
2a R'=-CH_3	134-136/1	73	2,3 (s,3H)CH_3; 4,1(bd,2H)NH_2-; 6,4 - 7,5(m,4H)Ø-H
2b R'= -C_2H_5	142-144/1	30	1,5(t,J=10 Hz,3H)-CH_3; 2,7(q,J=10 Hz,2H)-CH_2-; 4,2(bd,2H)-NH_2; 6,4 - 7,7(m,4H) Ø-H
3a2 R'=-CH_3	102-103	75	2,3(s,3H)CH_3CO; 2,5(s,3H)CH_3Se-; 7,3 - 7,8(m,4H)Ø-H et 9,6(bd,1H)-NH-
3b2 R'=-C_2H_5	81	63	1,5(t,J=8 Hz,3H)CH_3-; 2,6(q,J=8 Hz,2H)-CH_2-; 6,3 - 8,3(m,5H)Ø-H and -NH-
4a1	125-28/11 litt.[9] 154/45	21	5,98 - 8,27(m,4H)Het. H; 9,67 (s,1H)C_2-H
4b1	95-96	2 (c)	6,80 - 8,20(m,4H) Het. H; 11,3(s,1H) H_2
4a2	130-132/11 litt.[10] 140/51	25	2,66(s,3H)-CH_3; 6,96 - 7,93(m,4H)Het. H
4b2	106-107	11	2,76(s,3H)CH_3-; 7,20 - 8,10(m,4H)Het. H
4a3	117-120 litt.[11] 117	33	6,92 - 7,36(m,5H)Ø-H; 7,56 - 7,92(m,4H)Het. H
4b3	118-120	15	6,73 - 7,39(m,5H)Ø-H; 7,49 - 8,09(m,4H)Het. H
4a4	40-41	24	1,53(t,3H,J=6,9 Hz)CH_3-; 4,48(q,2H,J=6,9 Hz)-CH_2-; 7,02 - 8,19(m,4H)Het. H
4b4	74	13	1,29(t,3H,J=6,8 Hz)CH_3-; 4,30(q,2H,J=6,8 Hz)-CH_2-; 6,88 - 8,29(m)Het. H
4a5	116	27	6,66 - 7,32(m,5H)Ø-H; 7,68 - 8,44(m,4H)Het. H
4b5	76-80	2	6,86 - 7,45(m,5H)Ø-H; 7,69 - 8,41(m,4H)Het. H

(a) All the new products were characterized by I.R., ^1H and ^{13}C N.M.R. and mass spectrometry.

(b) Yields of pure and isolated products were calculated from anilines **2**.

(c) This product is air and light sensitive.

(d) The N.M.R. spectra were obtained on a Varian T 60 using $CDCl_3$ as solvent. Chemical shifts are given relative to H.M.D.S.O. as internal reference (s = singlet, t = triplet, q = quadruplet, m = massif, bd = broad)

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12. The fundamental heterocycle **4bl** gives the following low resolution (70 eV) mass spectra

233 : $C_7H_5NTe^{\cdot +}$ (100 %) - 206 : $C_6H_4Te^{\cdot +}$ (79 %) - 167 : C_3HTe^{+} (5 %) - 156 : $C_2H_2Te^{\cdot +}$ (3 %) - 155 : C_2HTe^{+} (4 %) - 130 : Te^{+} (30 %) - 103 : $C_7H_5N^{\cdot +}$ (5 %) - 102 : $C_7H_4N^{+}$ (6 %) - 76 : $C_6H_4^{\cdot +}$ (75 %)

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