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SYNTHESIS OF TETRAHYDROSELENO-1 AND TELLURO-1 PYRANONES-4 (*)

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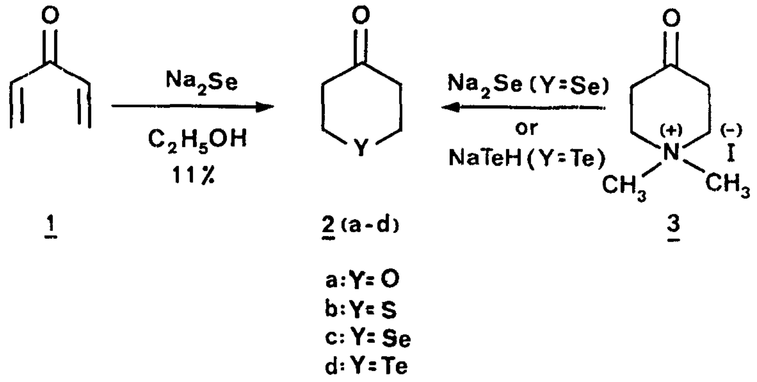
Abstract :

The synthesis of the unsubstituted tetrahydroseleno-1-pyranone-4 and its telluro analog is described, as well as some of their physical properties.

Tetrahydroseleno-1-pyranone-4 derivatives are known for a few years[1(a-d)] but the parent heterocycle 2c has not been synthetized till now(**). This compound represents a possible key step for the synthesis of monocyclic diselenopyranylidene derivatives, one of selenium π-donor system for the synthesis of organic metals. In our hands, the Dieckmann cyclisation of the diethylester of seleno-3,3'-dipropanoic acid under various experimental conditions did not furnished the ethoxycarbonyl-3-seleno-1-pyranone-4 which might be expected to lead to 2c after saponification and decarboxylation. The reaction of Na_2Se in ethanolic solution with divinylketone 1 affords 2c with a poor yield (11 %). However, we have observed that the reaction of an aqueous solution of Na_2Se on 1,1-dimethyl-4-piperidonium iodide 3 and in presence of diethylether leads to 2c with a good yield (61 %). This synthesis, analogous to the work of JOHNSON[2a] and UNKOVSKII[2b] in the case of the thio analog 2b has also been successfully applied to the elaboration of the quite unstable [3] tellura-1-cyclohexanone-4 2d (38 % yield), starting from 3 and NaTeH.
This last result represents the first example of a telluro-1-pyranone-4 system.
The two new heterocycles 2c and 2d have been fully characterized by mass spectrometry, I.R., ^1H-NMR and ^{13}C-NMR spectroscopies[4(a-d)].

Possessing now the four unsubstituted tetrahydrochalcogeno-1-pyranones-4 2(a-d)[5], we have observed, as expected, a linear correlation between the ^{13}C-NMR chemical shift of the C_2 carbon atom of all the members 2(a-d) of this family of heterocycles and the C_2 carbon atom of various molecules such as :

-chalcogena cyclohexanes [6a] : $\delta\ ^{13}C\ C_2(4) = 0.98\ \delta\ ^{13}C\ C_2\ (3) + 2.15$ (r = 0.995)
-chalcogena-1-chromanones-4 [6b] : $\delta^{13}C\ C_2(5) = 0.96\ \delta^{13}C\ C_2(3) - 0.35$ (r = 0.989)
-dimethylchalcogenides [6(c-f)] : $\delta^{13}C\ (6) = 1.07\ \delta\ ^{13}C\ C_2\ (3) - 12.67$ (r = 0.997)



Scheme 1

Furthermore, a linear correlation is also observed between the δ ^{13}C chemical shift of the C_2 carbon atom of 2(a-d) and the electronegativity (Ey) of the heteroatom : $\delta^{13}C$ C_2 (2) = 51.8 Ey - 108.4 (r = 0.973). Other ^{13}C NMR chemical shifts represent valuable data for the study of the conformation of this kind of heterocycles and the effect of the replacement of a methylene group in the cyclohexane ring, by a chalcogen atom, which are still widely studied problems [1b, 6(a,g)].

<u>References and notes</u> :

(*) Part of this work has been presented as a poster at the "Xth European Colloquium on Heterocyclic Chemistry", 1-3 October 1984, Kaiserslautern.

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3. Compound 2d seems to be quite unstable and must be stored in the cold, in the dark and in solution otherwise loss of tellurium is observed.
4.a. 70 eV low resolution mass spectrum of 2c : m/z : 164 (^{80}Se) $M^{\cdot+}$: 85 %; 136 (^{80}Se) $m-28]^{\cdot+}$: 41 %; 108(^{80}Se) $M-CO-C_2H_4]^{\cdot+}$: 100 %; 94 (^{80}Se) $M-70]^{\cdot+}$: 21 % and of 2d ; m/z : 214 (^{130}Te) $\overline{M}]^{\cdot+}$: 100 %; 186 (^{130}Te) $M-28]^{\cdot+}$: 35 %; 158 (^{130}Te) : $M-CO-C_2H_4]^{\cdot+}$: 36 %; 144 (^{130}Te) : $M-70]^{\cdot+}$: 48 %; 130 (^{130}Te) : $Te]^{\cdot+}$: 28 %.
  b. 2c $\nu_{C=0}$ (KBr) 1710 cm^{-1}; 2d $\nu_{C=0}$ (CCl_4) : 1705 cm^{-1}
  c. δ ^{1}H-NMR (ppm/HMDS) in solution in $CDCl_3$ 2c and 2d symmetrical multiplet centered respectively at 2.70 and 2.82 ppm.
  d. δ ^{13}C-NMR (ppm/TMS): 2c: C_2: 19.2; C_3: 43.6; C_4: 209.4; 2d: C_2: -6.0; C_3: 43.5; C_4: 211.2
5. Compounds 2a and 2b are commercially available from Aldrich and Co.
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(**) <u>Note added in proof</u>
During the modification of the text consecutive to the first submission, a similar reaction for the selenium derivative was published by M.D. THOMPSON and Al. in J. Org. Chem. 50 (1985) 2580.

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