

3,4-Dihydro-1*H*-2-benzothiin-3-one, 3,4-Dihydro-1*H*-2-benzoselenin-3-one
and 3,4-Dihydro-1*H*-2-benzotellurin-3-one

Ch. Lemaire (a), A. Luxen (a), L. Christiaens* (a) and M. Guillaume (b)

(a) Institute of Organic Chemistry, B.6., University of Liège, Sart-Tilman,
4000 Liège, Belgium

(b) Centre de Recherches du Cyclotron, B.30., University of Liège, Sart-Tilman,
4000 Liège, Belgium

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The synthesis of 3,4-dihydro-1*H*-benzothiin-3-one and its selenium and tellurium analogs is reported from *o*-bromomethylphenylacetyl chloride and sodium hydrogen chalcogenates, *via* phase-transfer catalysis.

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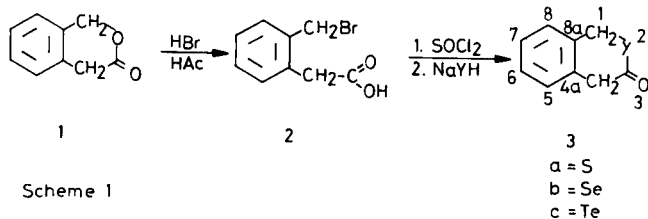
In the course of our efforts to synthesize new fundamental heterocyclic systems, we recently reported a new synthesis of chalcogenolactones *via* a two-phased tetrabutylammonium hydrogen sulfate catalysed condensation of halogen substituted acid chlorides with sodium hydrogen chalcogenides (1).

In this work, we can generalize this reaction to the synthesis of the hitherto unknown 3,4-dihydro-1*H*-2-benzothiin-3-one (**3a**) (isothiochroman-3-one), 3,4-dihydro-1*H*-2-benzoselenin-3-one (**3b**) (isoselenochroman-3-one) and 3,4-dihydro-1*H*-2-benzotellurin-3-one (**3c**) (isotellurochroman-3-one). The starting material, *o*-bromomethylphenylacetic acid (**2**) is obtained *via* a ring-opening hydrolysis of isochroman-3-one (**1**) with hydrobromic acid in acetic acid. It is identical with the product described by another method (2). In a one pot reaction, the corresponding acid chloride has been cyclized by sodium hydrogen chalcogenide to the attempted thio, seleno and telluro lactones (**3**), with moderate to good yields (Scheme 1). The three new fundamental heterocyclic systems were characterized by elemental analysis (Table 1), ir, ¹H and ¹³C nmr spectroscopy (Table 2) and by mass spectrometry (Scheme 2).

The δ ¹³C chemical shift of C₁ and C₄ follow the same evolution demonstrated in earlier observations for the corresponding carbons of chalcogenacetates (**3**). Assignment of C₁ is made on the basis of a linear correlation of its δ

Table 1

Product	Mp °C	Yield (%)	Empirical formula	Calcd.		Found	
				C	H	C	H
3a	105-106	58	C ₈ H ₈ OS	65.85	4.87	65.8	4.9
3b	111-114	56	C ₈ H ₈ OSe	51.18	3.79	51.0	4.0
3c	112-115	60	C ₈ H ₈ OTe	41.60	3.08	not realized	



Scheme 1

Scheme 2: Main fragmentations of the heterocycles 1 and 3a-c

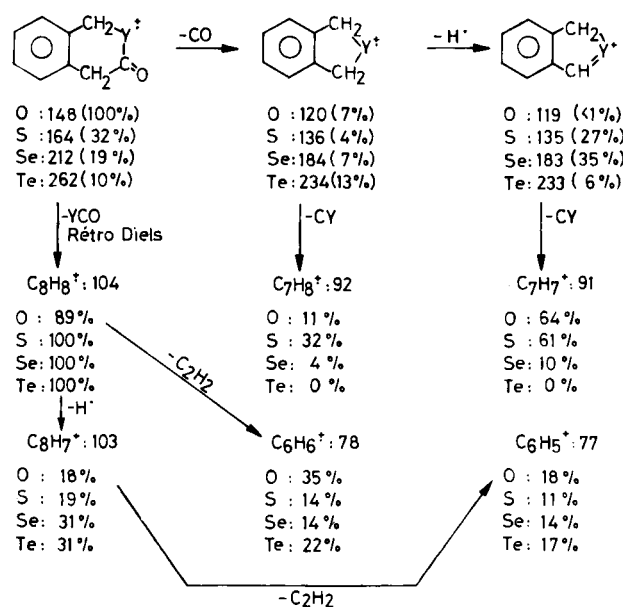


Table 2

IR, ¹H and ¹³C NMR (δ) Values (in ppm) for the Heterocycles 1 and 3

	O (1)	S (3a)	Se (3b)	Te (3c)
ν C=O	1748	1652 1660 1665	1665	1655
H ₁ (s)	5.2	4.1	4.2 (J ⁷⁷ Se—H ₂ = 15 Hz)	4.3 (J ¹²⁵ Te—H ₂ = 31.5 Hz)
H ₄ (s)	3.6	3.7	3.7	3.7
C=O	169.3	202.4	206.4	209.6
C ₁	69.9	34.1	27.7	8.5
C ₄	35.9	49.2	52.5	58.1
C ₅ —C ₆	124.2	126.6	126.5	126.3
	126.9	127.4	127.3	127.5
	128.5	127.9	127.5	128.5
		128.6	129.2	129.7
C _{4a} —C _{8a}	130.6	133.7	133.5	132.9
	131.2	134.2	135.9	138.4

^{13}C , within the chalcogen series, compared with the δ $^{13}\text{CH}_2$ of dibenzylchalcogenides (4). The mass spectrometry shows the attempted molecular ion, with the correct isotopic ratio for one selenium or one tellurium by molecules. The fragmentation of the sulfur, selenium and tellurium new ring systems is compared (Scheme 2) with the fragmentation of the oxygen analog (1)

EXPERIMENTAL

The ir spectra were determined on a Beckman ir 20 A apparatus in 1% potassium bromide pellets. The ^1H nmr spectra were recorded on a Varian T 60 apparatus in deuteriochloroform with hexamethyldisiloxan as internal standard. The ^{13}C nmr values were obtained from a Bruker HFX 90 in deuteriochloroform and the values are given with respect to TMS. Mass spectra were determined on a Varian MAT 112 apparatus at 70 eV with direct introduction.

1. Synthesis of *o*-Bromomethylphenylacetic Acid (2).

A solution of 2.4 g (16 mmoles) of lactone 1 in 20 ml of a 33% solution of hydrobromic acid in acetic acid was maintained at 20° for two hours and then at 70° for an hour. Dilution with cold water (50 ml) and filtration affords the acid 2 which was air dried (mp 139-141°, lit (2) 129-132°) and used crude in the following reaction.

2. General Procedure for the Preparation of Lactones 3.

Acid 2 (0.9 g, 4 mmoles) was refluxed in 5 ml of thionyl chloride. After careful elimination of this reagent under vacuum, the crude acid chloride was dissolved in 5 ml of dry toluene and slowly added to a solution of 4 mmoles of sodium hydrogen chalcogenide in 15 ml of water (generated from 4 mmoles of chalcogen and 8.1 mmoles (0.31 g) of sodium borohydride) and containing 0.3 g of tetrabutylammonium hydrogen sulfate. The mixture was stirred at room temperature for 4 hours. After washing with 10% aqueous sodium carbonate and drying, the toluene was removed under reduced pressure and the residual solid was recrystallised from a ligroin-benzene mixture.

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