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## SPECTROSCOPIC INVESTIGATIONS

### XVII \*. $^{77}\text{Se}$ AND $^{125}\text{Te}$ NMR RESONANCES OF SOME SELENOL AND TELLUROL ESTERS \*\*

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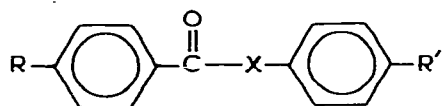
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#### Summary

In this paper the first directly determined  $^{77}\text{Se}$  or  $^{125}\text{Te}$  NMR chemical shifts of Se- and Te-aryl esters of three aromatic carboxylic acids are presented and discussed.

In contrast to extensive  $^{77}\text{Se}$  NMR studies of various organoselenium compounds [1–4], to our knowledge only a few publications have appeared [5,6] in which  $^{125}\text{Te}$  NMR data for organotellurium compounds are reported and those tellurium chemical shifts were determined indirectly by using heteronuclear magnetic double resonance experiments.

In connection with our recently started investigations on the mass spectro-



(Ia–Ic, X = Se)

(IIa–IIc, X = Te)

(a: R = H, R' = CH<sub>3</sub>;

b: R = CH<sub>3</sub>O, R' = CH<sub>3</sub>;

c: R = C<sub>8</sub>H<sub>17</sub>O, R' = C<sub>5</sub>H<sub>11</sub>)

\* For Part XVI see ref. 22; simultaneously Part IX in the series on Organic Selenium Compounds (for Part VIII see ref. 23) and Part V in the series on Organic Tellurium Compounds (for Part IV see ref. 24).

\*\* Dedicated to Prof. Dr. phil. A. Schönberg on the occasion of his 86th birthday.

TABLE 1

 $^{77}\text{Se}$  AND  $^{125}\text{Te}$  NMR DATA FOR SOME SELENOL AND TELLUROL ESTERS OF TYPE I AND II

Compound	$\nu(^{77}\text{Se})$ (Hz)	$\delta(^{77}\text{Se})$ (ppm <sup>a</sup> )	$\nu(^{125}\text{Te})$ (Hz)	$\delta(^{125}\text{Te})$ (ppm <sup>a</sup> )
Ia	3005.1	157.4		
Ib	2763.7	144.8		
Ic	2733.1	143.2		
IIa			15867.6	502.4
IIb			15085.5	477.7
IIc			14935.0	472.9

<sup>a</sup> To low field of (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Se)<sub>2</sub> ( $\delta(^{77}\text{Se}) = 0$  ppm, absolute frequency: 19.0921277 MHz) or (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Te)<sub>2</sub>, respectively, ( $\delta(^{125}\text{Te}) = 0$  ppm, absolute frequency: 31.5823970 MHz).

meric [7,8], photochemical [8–14], and, in particular, liquid-crystalline [15, 16] behaviour of selenol and tellurol esters, we have prepared the Se- and Te-aryl esters, Ia–Ic and IIa–IIc, of three seleno- and telluro-benzoic acids with different *para*-substituents.

The liquid-crystalline properties of the two new compounds, Ic and IIc, will be discussed elsewhere in comparison with their isoelectronic O- and S-analogues [8]. In Table 1 we present the  $^{77}\text{Se}$  and  $^{125}\text{Te}$  chemical shifts of the six esters, Ia–Ic and IIa–IIc, containing  $^{77}\text{Se}$  and  $^{125}\text{Te}$ , respectively, in natural abundance. These NMR data are to our knowledge not only the first provided for both classes of compounds, but also among the first  $^{125}\text{Te}$  resonances observed directly for any compound [25].

The NMR data recorded in Table 1 for three Se- and Te-aryl esters each display similar features, as expected. The smaller chemical shifts for the two *para*-alkoxy substituted esters b and c relative to a in both series suggest that the selenium and tellurium nuclei are strongly shielded by the electron density donated by the *para*-alkoxy groups. It is interesting to note that both hetero atoms are thus affected even with a carbonyl function between them and the *para*-alkoxy substituted aromatic ring. Similar and even more pronounced effects in the same direction are known for the somewhat related *para*-methyl substituted diaryl ditellurids [6].

Our findings encourage us to study effects of various substituents in different positions of both phenyl rings of selenol and tellurol esters of type I and II in more detail on the  $^{77}\text{Se}$  or  $^{125}\text{Te}$  chemical shifts of I and II, respectively.

## Experimental

The  $^{77}\text{Se}$  and  $^{125}\text{Te}$  NMR measurements were carried out on a Varian XL-100-15 spectrometer operating in pulsed Fourier transform mode. The 19.09 MHz and 31.59 MHz observing frequencies were derived from the Gyrocode decoupler with the aid of Gyrocode observe modification [17]. These frequencies were applied to a V-4415 probe equipped with a home-built frequency-tuned component for the observation and internal  $^2\text{H}$  lock (15.40 MHz) frequencies. These decoupling experiments were performed at 33°C by means of a Schomandl MS 100 M frequency synthesizer and an ENI model 310 L

broadband rf power amplifier. The samples were dissolved in deuteriochloroform, at concentrations of 300 mg compound in 2.5 ml solvent and placed in 12-mm-o.d. tubes. IR spectra: Beckman IR-9.  $^1\text{H}$  NMR spectra: Varian HA-100; tetramethylsilane as internal standard. Mass spectra: Varian MAT-711; electron energy 70 eV; the temperature of evaporation are given in parentheses; the reported mass units are based on the isotopes  $^{80}\text{Se}$  or  $^{130}\text{Te}$ , respectively. Melting points: Büchi SMP-20 or copper block, uncorrected.

With the exception of Ic, IIc and bis(4-pentylphenyl) ditelluride all other organoselenium and organotellurium compounds used in this study have been described in the literature: Ia [18], Ib [15], IIa and IIb [14], bis(4-methylphenyl) diselenide [19] and bis(4-methylphenyl) ditelluride [20]. Satisfactory melting points, elemental analyses and spectroscopic data were taken as criteria of their purity.

Ic and IIc which are described below have to be stored in the dark under nitrogen or argon at low temperature because of their sensitivity to heat, air, moisture, and light.

#### *Se-4-Pentyl-4-octyloxyselenobenzoate (Ic)*

The organoselenium compound available by reaction of powdered selenium (8.29 g, 0.105 g-atom) with the Grignard compound from 1-bromo-4-pentylbenzene (22.71 g, 0.1 mol) and magnesium (2.55 g, 0.105 g-atom) was prepared in 100 ml dry ether. The solution thus obtained is directly treated with 4-octyloxybenzoyl chloride (28.22 g, 0.105 mol) in 100 ml dry ether. The procedure, an improved version of an older one [18], is described in detail in ref. 15. After the usual work-up [15] the crude product obtained was purified by three subsequent column chromatographic purifications (600, 150, and 150 g silica gel; diameters: 0.2 mm), elution with light petroleum ether/methylene chloride (1/1). After recrystallisation from hexane, the yield was 7.2 g (16% based upon 1-bromo-4-pentylbenzene) Ic, colourless needles with m.p.  $55^\circ\text{C}$ . IR ( $\text{CCl}_4$ ):  $\nu(\text{C}=\text{O})$   $1690\text{ cm}^{-1}$ . Mass spectrum ( $90^\circ\text{C}$ ):  $m/e$  460 ( $^{80}\text{Se}-M^+$ ,  $\sim 0.1\%$ ), 432 ( $M^+ - \text{CO}$ ,  $<1\%$ ), 352 ( $\text{C}_{25}\text{H}_{36}\text{O}$ ,  $\sim 0.1\%$ ), 234 (18%), 233 ( $\text{C}_{15}\text{H}_{21}\text{O}_2$ , 100%), 121 ( $\text{C}_7\text{H}_5\text{O}_2$ , 50%).  $^1\text{H}$  NMR ( $\text{CCl}_4$ ): aliph. H m 0.8–1.9, Ar- $\text{CH}_2$  t ( $J \sim 7\text{ Hz}$ ) 2.61, Ar-O $\text{CH}_2$  t ( $J \sim 7\text{ Hz}$ ) 3.95, Ar-H 2d ( $J \sim 9\text{ Hz}$ ) 6.83 and 7.83, and 2d ( $J \sim 8\text{ Hz}$ ) 7.12 and 7.38 ppm both doublet pairs as parts of 2 AA'BB' systems; proton ratio 12/1/1/1/1/1/1. Elemental analysis: Found: C, 67.91; H, 8.09.  $\text{C}_{26}\text{H}_{36}\text{O}_2\text{Se}$  (459.5) calcd.: C, 67.96; H, 7.90%.

#### *Bis(4-pentylphenyl) ditelluride*

The Grignard compound prepared from 1-bromo-4-pentylbenzene (90.85 g, 0.4 mol) and magnesium (9.72 g, 0.4 g-atom) in 400 ml dry tetrahydrofuran was treated with powdered tellurium (51.04 g, 0.4 g-atom) and oxidized with air overnight in principle similar to a published procedure [20]. The usual work-up [20], extraction with 1 l ether, several filtrations of the ethereal phase through silica gel yielded, upon evaporation of the ether, 101.4 g (92%) partly crystalline ditelluride. This material still contained traces of elementary tellurium which were impossible to remove completely, neither by column chromatography on silica gel nor by crystallisation (thermally unstable?). For analytical purposes a sample of this ditelluride was drained on a piece of clay. Deep

red leaflets with m.p. 29°C. Mass spectrum (room temp.):  $m/e$  554 ( $^{130}\text{Te}_2\text{-M}^+$ , 1%), 424 ( $\text{M}^+ - ^{130}\text{Te}$ , 3%), 294 ( $\text{M}^+ - ^{130}\text{Te}_2$ , 2%), 277 ( $\text{M}^+/2$ , 3%), 91 ( $\text{C}_7\text{H}_7$ , 100%).  $^1\text{H NMR}$  ( $\text{CCl}_4$ ): aliph. H m 0.8–1.8, Ar- $\text{CH}_2$  t ( $J \sim 7$  Hz) 2.58, Ar-H 2d ( $J \sim 8$  Hz) 6.93 and 7.63 ppm as parts of an AA'BB' system: proton ratio 9/2/2/2. Elemental analysis: Found: C, 48.00; H, 5.66.  $\text{C}_{22}\text{H}_{30}\text{Te}_2$  (549.7) calcd.: C, 48.07; H, 5.50%.

#### *Te-4-Pentyl-4-octyloxytellurobenzoate (IIc)*

The preparation was carried out according to a modified version [14] of a procedure published by Renson et al. [21]: Bis(4-pentylphenyl) ditelluride (27.49 g, 0.05 mol) dissolved in 60 ml ethanol and 30 ml benzene was reduced with sodium borohydride (4.54 g, 0.12 mol) in 100 ml 0.1 *N* aqueous sodium hydroxide. The mixture was covered with a layer of ether (250 ml) and then 4-octyloxybenzoyl chloride (32.25 g, 0.12 mol), dissolved in 50 ml of ether, was added dropwise. After the usual work-up [14] we found the following purification procedure advantageous: 2 g batches of the crude tellurol ester were dissolved in 25 ml methylene chloride/petroleum ether (1/3) and filtered through a chromatographic column (diameter: 2 cm; height of the silica gel (diameter: 0.2 mm) zone: 10 cm) within approximately 30 sec under vacuum of a water suction pump. The solvent was now removed in a rotation evaporator below 50°C and the residue was recrystallized from hexane under argon. The overall yield was 31.7 g (62% based upon the ditelluride) IIc, lemon yellow leaflets with m.p. 41°C. IR ( $\text{CCl}_4$ ):  $\nu(\text{C}=\text{O})$  1682  $\text{cm}^{-1}$ . Mass spectrum (110°C):  $m/e$  510 ( $^{130}\text{Te-M}^+$ ,  $\sim 0.1\%$ ), 482 ( $\text{M}^+ - \text{CO}$ , 5%), 352 ( $\text{C}_{25}\text{H}_{36}\text{O}$ , 1%), 234 (22%), 233 ( $\text{C}_{15}\text{H}_{21}\text{O}_2$ , 100%), 121 ( $\text{C}_7\text{H}_5\text{O}_2$ , 65%).  $^1\text{H NMR}$  ( $\text{CCl}_4$ ): aliph. H m 0.8–1.9, Ar- $\text{CH}_2$  t ( $J \sim 7$  Hz) 2.62, Ar-O $\text{CH}_2$  t ( $J \sim 7$  Hz) 3.94, Ar-H 2d ( $J \sim 9$  Hz) 6.83 and 7.64, and 2d ( $J \sim 8$  Hz) 7.07 and 7.59 ppm both doublet pairs as parts of 2 AA'BB' systems; proton ratio 12/1/1/1/1/1. Elemental analysis: Found: C, 61.51; H, 7.11%.  $\text{C}_{26}\text{H}_{36}\text{O}_2\text{Te}$  (508.2) calcd.: C, 61.45; H, 7.14%.

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