Short Communication

Cyclic aryleneazachalcogenenes

IV^a. Gas chromatographic properties of polyfluorinated 2,1,3-benzoselenadiazoles

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ABSTRACT

Polysubstitution of hydrogen atoms in 2,1,3-benzoselenadiazoles (piaselenoles), used in the determination of selenium by gas chromatography with electron-capture detection (GC–ECD), by fluorine atoms raises the sensitivity of a ^{63}Ni electron-capture detector to substances by more than an order of magnitude, without reducing their high volatility. The corresponding polyfluorinated 1,2-diaminobenzenes react quantitatively with Se(IV) derivatives in aqueous acidic media and the selenadiazoles formed are effectively extracted with 1 ml of toluene from 500 ml of solution. Thus, polyfluorinated 1,2-diaminobenzenes potentially form a new group of analytical reagents for the GC–ECD determination of selenium.

INTRODUCTION

Important biological and medical functions of selenium [2] make the development of new method for its determination, and the improvement of known methods, highly desirable.

For the determination of selenium at the ultra-trace level by gas chromatography with electron-capture detection (GC–ECD) a convenient analyte form is the 2,1,3-benzoselenadiazoles (piaselenoles), obtained by the reaction of Se(IV) with 1,2-diaminobenzenes in acidic media (for a review see ref. 3). In this determination, derivatives with a fluorine atom or trifluoromethyl group have advantages over other compounds owing to the shorter relative retention times (t_R) and lower detection limits [4,5].

The next logical step in this direction is the use of polyfluorinated derivatives. As reported [6], the reaction of selenious acid with 1,2-diamino-3,4,5,6-tetrafluoro-

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^{a} For part III, see ref. 1.

benzene leads to 4,5,6,7-tetrafluoro-2,1,3-benzoselenadiazole, which forms a synthetic background for the use of polyfluorinated 2,1,3-benzoselenadiazoles in the GC–ECD determination of selenium. However, neither the GC properties of these compounds nor the efficiency of their extraction from acidic media by organic solvents before injection into the chromatograph have been investigated. In addition, polyfluorinated 2,1,3-benzoselenadiazoles may have advantages over their hydrocarbon analogues owing to the high volatility [7], high electron affinity [8] and hydrophobicity (oleophilicity) [7] inherent in polyfluoroaromatic compounds.

In this work, we carried out comparative studies of the GC properties of 4,5,6,7-tetrafluoro-2,1,3-benzoselenadiazole (**1**) and 6-trifluoromethyl-4,5,7-trifluoro-2,1,3-benzoselenadiazole (**2**) *vs.* 5-trifluoromethyl-2,1,3-benzoselenadiazole (**3**), the most volatile compound among those investigated earlier and having one of the lowest detection limits [3–5]. We also performed a model experiment to detect 10^{-8} g-atom (0.79 μg) of selenium in 500 ml of water using 1,2-diamino-3,4,5,6-tetrafluorobenzene (**4**), a counterpart of compound **1**.
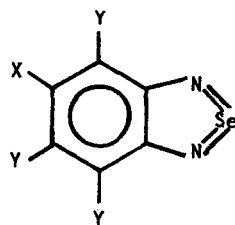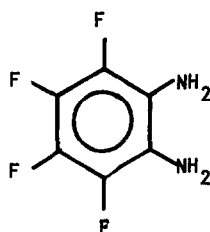
EXPERIMENTAL

Instrumentation

The GC measurements were carried out on a Model 3700 chromatograph (a complete copy of the Varian 3700 instrument produced in the USSR under Varian licence), using glass columns (2 m × 3.5 mm I.D.; Institute of Organic Chemistry, Novosibirsk, USSR) packed with SE-30 (5%) on Chromaton N AW DMCS or XE-60 (5%) on Chromaton N AW (LaChema, Czechoslovakia), a ^{63}Ni electron-capture detector and an Interchrom-1 electronic integrator. The injector and detector temperatures were 220°C and the column temperature was 130°C (isothermal). The working gas in the detector and the carrier gas were nitrogen. The carrier gas flow-rate was 50 ml/min. Toluene solutions of 10^{-5}–10^{-6} mol/l concentration were used, with an injection volume of 2 μl.

The ^{1}H, ^{19}F and ^{77}Se NMR spectra of compound **3** were measured on a Bruker AM-400 spectrometer at 400.134, 376.479 and 76.312 MHz, respectively, as C^{2}HCl$_3$ solutions (standards: internal, tetramethylsilane and perfluorobenzene; external, dimethyl selenide). Mass spectra were measured on a Finnigan MAT MS-8200 instrument (electron impact; 70 eV). UV–visible spectra were recorded on a Specord UV–VIS spectrophotometer as ethanol solutions.

Substances

Compounds **1**, **2** and **4** were synthesized and purified according to ref. 1. Compound **3** was obtained by a modified procedure [1] as follows. A solution of 2.21 g (0.01 mol) selenium tetrachloride in 20 ml of monoglyme was added dropwise in an argon atmosphere at 0°C to a stirred suspension of 2.49 g (0.01 mol) of 1,2-diamino-4-trifluoromethylbenzene dihydrochloride and 4.74 g (0.06 mol) of pyridine in 25 ml of monoglyme. Stirring was continued for 0.5 h, the solution was filtered, the solvent distilled off at reduced pressure and the residue recrystallized from hexane and sublimed in vacuum. Compound **3**, colourless crystals, yield 2.13 g (85%), m.p. 90–91°C (lit. [4] m.p., 91°C). Mass spectrum, M^+ (*m/z*, relative intensity), measured (calculated): 251.9422, 100% (251.9413). NMR spectra (δ, ppm): ^1H, 8.03 s, 7.78 d (^3J = 9.5 Hz), 7.46 d (^3J = 9.5 Hz); ^{19}F, 98.19 s; ^{77}Se, 1545 s. UV–VIS spectrum [λ_{max}, nm, (log ε)]: 334 (4.30),238 (3.89).

The purity of all compounds was monitored by GC using ECD and flame ionization detection.

Solutions for model experiment on the detection of selenium in water

A working solution of **4** was prepared by dissolving 0.45 g (2.5 · 10^{-3} mol) in 500 ml of hydrochloric acid.

A stock solution of selenium (IV) was prepared by dissolving 1.1096 g (0.01 mol) of selenium dioxide in 100 ml of distilled water. Working solutions were prepared by appropriate dilution.

Calibration solutions of **1** were obtained by dissolving 0.2550 g (1 · 10^{-3} mol) in 100 ml of toluene with subsequent appropriate dilution.

Model experiment procedure (modified procedure [9])

Aqueous selenium dioxide (500 ml), theoretically containing 0.79 μg (1 · 10^{-8} g-atom) of selenium, and 40 ml of concentrated hydrochloric acid were thoroughly mixed in a separating funnel. The solution was vigorously shaken with 25 ml of toluene until saturation. After phase separation, the aqueous phase was transferred to another separating funnel and 10 ml of the acidic solution of **4** were added. After 2 h, 1 ml of toluene was added and the mixture was vigorously shaken for 5 min. The toluene extract was separated and 2 μl were injected into the chromatograph (XE-60 column). The amount of selenium (IV) was determined by comparing the area of the peak of compound **1** in the chromatogram with that of the calibration solution of **1**. The results was avereged from a series of five repeated measurements.

RESULTS AND DISCUSSION

It has been established earlier that procedures based on piaselenoles and GC–ECD allow selenium determinations at the ultra-trace levels (1–10 ng/l). Selenadiazoles possessing the highest electron affinity (providing the lowest detection limits) contain bromine atoms or a nitro group, which reduce their volatility. On the other hand, more volatile selenadiazoles do not give such low detection limits because of the insufficient sensitivity of the electron-capture detector towards then [3–5].

We have found that the use of polyfluorinated 2,1,3-benzoselenadiazoles **1** and **2** makes it possible to combine high volatility with high electron-capture ability.

TABLE I

GAS CHROMATOGRAPHIC PROPERTIES OF POLYFLUORINATED 2,1,3-BENZOSELENA-
DIAZOLES 1–3 AND POLYFLUORINATED 1,2-DIAMINOBENZENE 4

Glass packed column, 2 m × 3.5 mm I.D., 130°C.

Compound	SE-30		XE-60	
	t_R	MS^a	t_R	MS^a
1	1.00	11.0	1.92	11.0
2	1.23	11.0	2.77	11.0
3	1.00	1.0	1.00	1.0
4	0.83	0.07	3.36	0.07

^{a} Relative standard deviation 10%.

Table I lists t_R values and the molar sensitivity (MS) of the ^{63}Ni electron-capture detector to compounds 1 and 2 measured relative to those of compound 3. Fig. 1 presents some typical chromatograms.

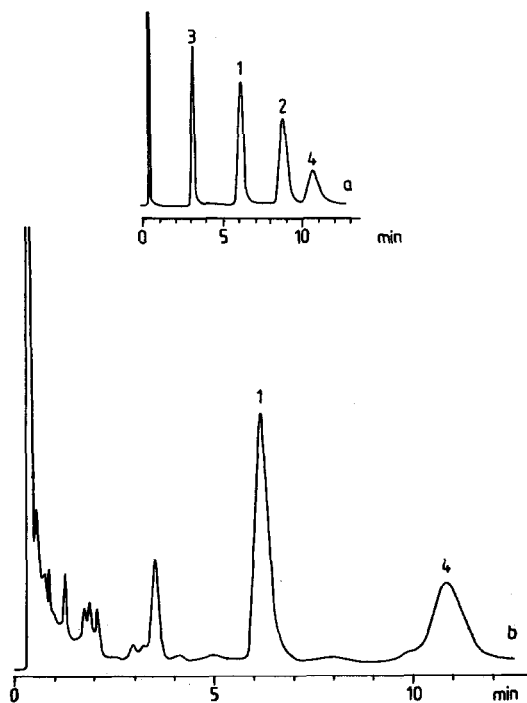It follows from Table I that the ECD sensitivity to compounds 1 and 2 exceeds

Fig. 1. Typical chromatograms. (a) Chromatogram of the toluene solution of a model mixture of compounds 1–4 (mole ratio 1:1:10:10, respectively); XE-60 column, 130°C. (b) Chromatogram of the toluene extract (1 ml) from aqueous acidic selenium dioxide solution (500 ml of water, 0.79 μg of selenium treated with a hydrochloric acid solution of compound 4; XE-60 column, 130°C.

to 3 by more than an order of magnitude. On the non-polar SE-30, the t_R values of 1 and 3 are the same, whereas that of 2 slightly exceeds them. On passing to the polar XE-60, the t_R values of 1 and 2 markedly increase, but the overall time of chromatographic analysis at the same column temperature as for SE-30 remains satisfactory (see Fig. 1).

The t_R of 4 on SE-30 is shorter than that of 1, but on passing to XE-60 this order is reversed (Table I). This creates an additional possibility. Although the MS towards 4 is low (Table I), the similarity of the t_R values of 4 and 1 and the use of a large molar excess of a diamine in standard procedures (10^2–10^4 [3–5,9]) hinder the recording of the peak of 1 aganist the background of the preceding peak of 4. For that reason, the excess of diamine is generally removed from the sample before injecting it into the chromatograph by washing it with an acid [3–5,9]. On the XE-60 column, the excess of diamine 4 does not hinder identification and peak intensity measurement of 1 (Fig. 1), and the washing operation to remove the excess may be omitted from the analytical procedure.

The efficiency of detection of selenium (IV) in aqueous solutions using 4 is also fairly high. In the model experiment, the efficiency of detecting $1 \cdot 10^{-8}$ g-atom (0.79 μg) of selenium in 500 ml of water using 4 at a molar excess of the latter of $5 \cdot 10^3$ was 80% (relative standard derivation = 10%) of the theoretical value (the conditions were not optimized). It should be noted that the real content of selenium (IV) in the model solution was smaller than the theoretical value (thermogravimetric standardization of the stock solution was not carried out; a chromatographic analysis error made it superfluous).

The results obtained suggest that 4 and 1,2-diamino-5-trifluoromethyl-3,4,6-trifluorobenzene (corresponding to 2) are potential analytical reagents for the GC–ECD determination of selenium. Compound 4 is slightly advantageous, which is associated not so much with its greater volatility as with its greater synthetic availability (see ref. 1 and references cited therein).

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