ACTA CHEMICA SCANDINAVICA 24 (1970) 2061–2064

Organic Selenium Compounds

XV.* Alkoxyselenocarbonylhydrazines (*O*-Alkyl Monoselenocarbazates)

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Se-Carboxymethyl *O*-alkyl diselenocarbonates were prepared from alkali metal *O*-alkyl diselenocarbonates and alkali metal chloroacetate. The carboxymethyl esters react with hydrazines to form (alkoxyselenocarbonyl)hydrazines and some representative examples of this hitherto unknown type of compound were prepared.

As part of comparative studies of organic sulfur and selenium compounds some selenium analogues of alkoxythiocarbonylhydrazines (*cf.* Ref. 1) have been prepared from [(alkoxyselenocarbonyl)seleno]acetic acids and hydrazines. Both the [(alkoxyselenocarbonyl)seleno]acetic acids (I) and the alkoxyselenocarbonylhydrazines can be prepared by methods similar to those used for the preparation of the corresponding sulfur compounds,[1] but because of the instability of the selenium compounds, conditions are much more

$RO-CSe-SeCH_2COOH$ (I)

Ia. $R=CH_3$
Ib. $R=C_2H_5$
Ic. $R=CH_3CH_2CH_2$
Id. $R=(CH_3)_2CH$

$R^1O-CSe-NR^2-NH_2$ (II)

IIa. $R^1=C_2H_5$; $R^2=H$
IIb. $R^1=C_2H_5$; $R^2=CH_3$

$R^1O-CSe-NH-NHR^2$ (III)

IIIa. $R^1=CH_3$; $R^2=(CH_3)_3C$
IIIb. $R^1=CH_3$; $R^2=C_6H_5$
IIIc. $R^1=C_2H_5$; $R^2=(CH_3)_3C$
IIId. $R^1=C_2H_5$; $R^2=C_6H_5$
IIIe. $R^1=C_2H_5$; $R^2=o\text{-}NO_2C_6H_4$
IIIf. $R^1=(CH_3)_2CH$; $R^2=(CH_3)_3C$
IIIg. $R^1=(CH_3)_2CH$; $R^2=C_6H_5$

* Part XIV: *Acta Chem. Scand.* **24** (1970) 2055.

critical. In fact, it requires considerable experience to prepare these compounds. The isolation of the derivatives of both unsubstituted hydrazine and methylhydrazine were successful only after a long series of negative results. In addition, to avoid high temperatures and access of air, one of the conditions for a successful preparation seems to be that all operations are carried out rapidly. As was the case with the corresponding sulfur compounds, methylhydrazine reacts to give exclusively a 1,1-disubstituted hydrazine (IIb), whereas phenylhydrazine and *tert*-butylhydrazine give the 1,2-derivatives (III). The 1,2-disubstituted hydrazines are considerably more stable than those with a free NH_2 group.

Like [(ethoxyselenocarbonyl)seleno]acetic acid,[2] the other [(alkoxyselenocarbonyl)seleno]acetic acids react with ammonia to form *O*-alkyl selenocarbamates (selenourethans), which can also be obtained from alkyl cyanates and hydrogen selenide.[3]

The infrared spectra of both the [(alkoxyselenocarbonyl)seleno]acetic acids and the (alkoxyselenocarbonyl)hydrazines will be discussed in forthcoming papers.[4,5]

EXPERIMENTAL

[(*Ethoxyselenocarbonyl*)*seleno*]*acetic acid* (Ib). Carbon diselenide (16 g) was dissolved in benzene (70 ml). The solution was diluted with 60 ml of abs. ethanol and a solution of potassium hydroxide (5.2 g) in abs. ethanol (65 ml) was added dropwise with cooling and stirring. Potassium *O*-ethyl diselenocarbonate ("potassium diselenoxanthate") precipitated as an orange-yellow solid on addition of 3 volumes of ether and was filtered off and dried. Yield 17 g (71 %).

The potassium salt (17 g) was dissolved in 150 ml of cold water and the equivalent amount of neutralized chloroacetic acid (67 mmol in 100 ml of water) was added dropwise with stirring and cooling. The solution was cooled in ice and brought to pH 1 by addition of conc. hydrochloric acid. The acid separated as a yellow oil which solidified on standing in a refrigerator (4°C). It was recrystallized from hexane, the temperature not being taken above 35°C. It was found that either heating to a higher temperature during dissolution, or cooling to a lower temperature during crystallization, gave a less pure product; this was also the case if pentane, rather than hexane, was used. Yield 12 g (66 %) of bright yellow crystals with m.p. 64–64.5°C. (Found: C 21.84; H 3.12; Se 57.90. Calc. for $C_5H_8O_3Se_2$: C 21.88; H 2.94; Se 57.70). The compound decomposes rapidly at room temperature but can be kept for several months in a refrigerator (4°C).

The *O*-methyl, *O*-propyl, and *O*-isopropyl derivatives were prepared in a similar manner. Since, however, conditions are critical, full details of the preparation of the methyl and isopropyl derivatives are given as follows.

[(*Methoxyselenocarbonyl*)*seleno*]*acetic acid* (Ia). Carbon diselenide (5.16 g) was dissolved in benzene (20 ml) and the solution was diluted with methanol (18 ml). A solution of potassium hydroxide (1.65 g) in methanol (20 ml) was added with cooling and stirring. On addition of 3 vol. of ether potassium *O*-methyl diselenocarbonate was precipitated as a yellow solid. Yield 4.5 g. This was dissolved in cold water (70 ml) and a little less than the equivalent amount of sodium chloroacetate (18 mmol) in water (40 ml) was added with cooling and stirring. The solution was cooled with ice and brought to pH 1 with conc. hydrochloric acid. The solution became turbid and some selenium precipitated. The filtered solution was kept for 24 h at 4°C, after which time a crystalline precipitate had separated. Yield of crude product 4.0 g. After drying, the solid was extracted with boiling pentane and the solution was decanted and cooled in dry ice-acetone. Yield, 1.8 g of a bright yellow crystalline product with m.p. 57.5–58°C. (Found: C 18.54; H 2.47. Calc. for $C_4H_6O_3Se_2$: C 18.46; H 2.31). Continued extraction yielded 1 g of a less pure product.

[(*Isopropoxyselenocarbonyl*)*seleno*]*acetic acid* (Id). Potassium *O*-isopropyl diselenocarbonate was prepared from carbon diselenide (1.4 g) dissolved in benzene (8 ml) to

Table 1. (Alkoxyselenocarbonyl)hydrazines, $R^1O-CSe-NR^2-NHR^3$.

R^1	R^2	R^3	Formula	M.p., °C	Analyses (C, H, N)		
Me	H	Bu^t	$C_6H_{14}N_2OSe$	112–113	Found: 34.49;	6.49;	13.14
					Calc.: 34.45;	5.70;	13.40
Me	H	Ph	$C_8H_{10}N_2OSe$	115–116	Found: 42.05;	4.50;	12.22
					Calc.: 41.93;	4.40;	12.22
Et	H	H	$C_3H_8N_2OSe$	30– 31	Found: 21.70;	4.97;	16.75
					Calc.: 21.56;	4.79;	16.80
Et	Me	H	$C_4H_{10}N_2OSe$	oil	Found: 26.12;	5.46	
					Calc.: 26.55;	5.57	
Et	H	Bu^t	$C_7H_{16}N_2OSe$	84–84.5	Found: 37.62;	7.34;	12.64
					Calc.: 37.70;	7.23;	12.55
Et	H	Ph	$C_9H_{12}N_2OSe$	96– 97	Found: 44.32;	5.00;	11.35
					Calc.: 44.44;	4.94;	11.52
Et	H	*o*-$NO_2C_6H_4$	$C_9H_{11}N_3O_3Se$	102–103	Found: 37.52;	4.12;	14.32
					Calc.: 37.50;	3.85;	14·59
Pr^i	H	Bu^t	$C_8H_{18}N_2OSe$	102–103	Found: 40.50;	7.67;	11.92
					Calc.: 40.51;	7.60;	11.81
Pr^i	H	Ph	$C_{10}H_{14}N_2OSe$	104–105	Found: 46.38;	5.27	
					Calc.: 46.69;	5.45	

which 2-propanol (8 ml), and a little less than the calculated amount of 1.5 M KOH in 2-propanol, were added. The potassium salt precipitated on addition of 3 vol. of ether to the solution (yield 1.65 g). This salt was dissolved in cold water (100 ml) and a 1 N aqueous solution of sodium chloroacetate was added dropwise with cooling and stirring. When a little less than the calculated amount (6 mmol) had been added, some selenium separated. This was filtered off and the solution was cooled with ice and brought to pH 1 with conc. hydrochloric acid. The solution became turbid and deep yellow but no precipitation took place. However, when the solution was kept for 24 h at 4°C a crystalline precipitate separated. It was isolated by filtration, dried and recrystallized from hexane-pentane to yield 70 % of bright yellow crystals with m.p. 55–56°C. (Found: C 25.21; H 3.87. Calc. for $C_6H_{10}O_3Se_2$: C 25.00; H 3.47).

[*(Propoxyselenocarbonyl)seleno*]*acetic acid* (Ic) was prepared in the same manner as Id. M.p. 47–48°C. (Found: C 25.12; H 3.53. Calc. for $C_6H_{10}O_3Se_2$: C 25.00; H 3.47).

(Ethoxyselenocarbonyl)hydrazine (IIa). a) A suspension of Ib (500 mg) in water (35 ml) was added with shaking at room temperature to a solution of hydrazine hydrate (1 g) in water (10 ml). The acid dissolved with a yellow colour which faded in the course of 3 min. The solution was then cooled with ice, brought to pH 5 and extracted with ether (3 × 15 ml). The ether solution was washed with 2 M $NaHCO_3$, dried (Na_2SO_4), and evaporated *in vacuo* without heating. The oily residue was sublimed *in vacuo* (1 mmHg, bath temperature 40°C), using a "cold finger", cooled with dry ice-acetone, as receiver.

The ethoxyselenocarbonyl derivatives of methylhydrazine (IIb) and *tert*-butylhydrazine (IIIc) were prepared in essentially the same manner. This method was also used for the preparation of the methoxy and isopropoxy derivatives, (IIIa and IIIf),

except that recrystallization from pentane was used for purification, instead of sublimation.

b) (Ethoxyselenocarbonyl)hydrazine was also prepared by a somewhat different procedure which gave a purer product: The acid Ib (550 mg) was dissolved in a solution of sodium hydroxide (80 mg) in ethanol (100 ml) and hydrazine hydrate (100 mg) was added. The solution was cooled with ice, filtered from a precipitate of sodium hydroselenoacetate and the solvent removed *in vacuo*. The residue was extracted with ether, and after drying (Na_2SO_4), most of the ether was removed *in vacuo*. Pentane was added and the solution cooled in dry ice-acetone. The colourless crystalline precipitate was isolated by centrifugation. The m.p. of the purest product isolated was 30—31°C. However, essentially pure products may have m.p. as low as 20°C.

(Methoxyselenocarbonyl)hydrazine and (isopropoxyselenocarbonyl)hydrazine seem to be very unstable. The oily products, obtained by the same method (a) as the ethyl derivative, rapidly turned red in air and satisfactory analyses could not be achieved.

IIa yields an *m*-nitrobenzylidene derivative which separates as yellow crystals from an ether solution of equivalent amounts of IIa and *m*-nitrobenzaldehyde (yield 98 %). The compound is almost insoluble in ether and was purified by extraction with boiling ether. M.p. 195—196°C. (Found: C 39.90; H 3.82; N 13.94. Calc. for $C_{10}H_{11}N_3O_3Se$: C 40.00; H 3.69; N 14.00).

1-Ethoxyselenocarbonyl-2-phenylhydrazine (IIId). Ib (200 mg) was dissolved in ether (15 ml) and excess phenylhydrazine was added at room temperature with shaking. After standing for a few minutes the solution was washed with 0.5 N hydrochloric acid and then with 2 M $NaHCO_3$. The dried (Na_2SO_4) ether solution was concentrated *in vacuo* to 1—2 ml. On addition of 7—8 ml of hexane a colourless crystalline precipitate separated and was isolated by centrifugation.

The other phenylhydrazides (IIIb and IIIg) were prepared in the same manner. The *o*-nitrophenylhydrazide (IIIe) was prepared in ethanolic solution and separated as yellow crystals when water was added slowly to the ice-cooled solution.

O-*Alkyl selenocarbamates* were prepared by dissolving the acids (Ia—d) in aqueous ammonia. After 1 h at 0°C the solution was adjusted to pH 5—6, saturated with NaCl, and extracted with ether. The ether was removed by evaporation and the residue recrystallized from pentane. Yields 60—80 %. The melting points were identical with those found for products prepared from alkyl cyanates and hydrogen selenide.[3]

Acknowledgment. We thank mag. scient. Kurt Berg for carrying out a preliminary exploration of the preparation of these compounds.

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Received December 17, 1969.