Preparative Methods for Dialkyl Dithioseleno- and Thiodiselenocarbonates

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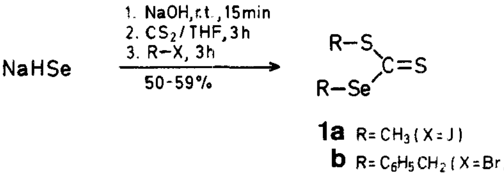
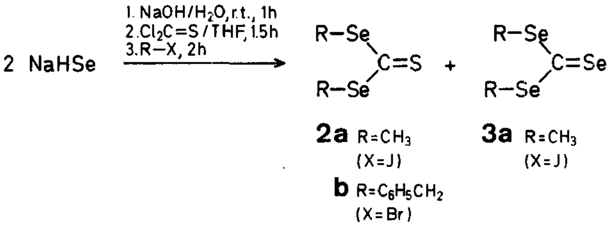
Preparative scale synthesis for *S,Se*-, *Se,Se'*- and *S,S'*-dialkyl (di)thioselenocarbonates **1**–**4** are described.

During the course of studies on heteroatom rearrangements[1], different types of dialkyl trithiocarbonates containing selenium in place of one or more sulfur atoms were needed for the synthesis of organoselenium model compounds. The synthetic procedures hitherto reported[2,3] have employed the difficultly accessible carbon diselenide, required a troublesome separation of some by-products, and have been, in particular, not suitable for large-scale preparations. Consequently, we report herein three convenient methods for their synthesis.

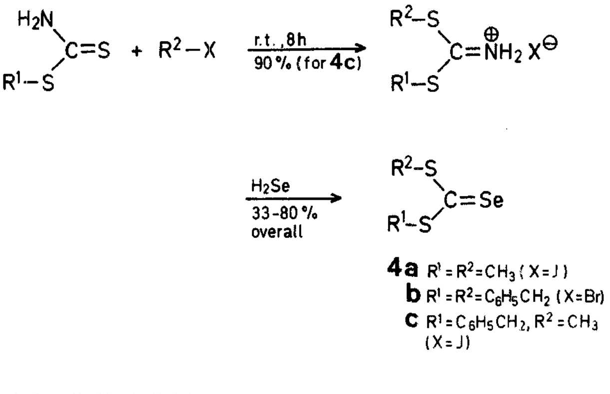
(*1*)



(*2*)



(*3*)



The *S,Se*-dialkyl dithioselenocarbonates **1** were prepared by the reaction (*1*) of sodium hydrogen selenide[4] with carbon disulfide followed by alkylation. The *Se,Se'*-dialkyl thiodiselenocarbonates **2** together with a small amount of dialkyl triselenocarbonate **3** were obtained from the reaction (*2*) of sodium hydrogen selenide with thiophosgene followed by alkylation. The *S,S'*-dialkyl dithioselenocarbonates **4** were prepared by the reaction (*3*) of hydrogen selenide with salts of *S,S'*-dialkyl iminodithiocarbonates, generated easily from alkyl dithiocarbamates and alkyl halides (Table).

It is interesting to note that in the preparation of **2**, a successive addition of thiophosgene and sodium hydroxide to the sodium hydrogen selenide gave **2** and **3** in 33% and 5% yields, respectively.

Table. Compounds **1**, **2**, **3**, and **4** prepared

Product	Yield [%]	Appearance	m.p. [°C] or b.p. [°C]/torr	Molecular Formula[a] or Lit. Data	I.R. ν[cm^{-1}]	^{1}H-N.M.R. (Solvent/TMS) δ[ppm]	M.S.[b] m/e (M$^+$)
1a	50	yellow oil	143°/19	m.p. −21 to −19 °C[2,3]	1090 (C=S); 1050 (C=S)	(CCl_4): 2.67 (s, 3H, $SeCH_3$)[c]; 2.73 (s, 3H, SCH_3)	186
1b	59	yellow needles	44–46°	$C_{15}H_{14}S_2Se$ (337.4)	1060 (C=S)	($CDCl_3$): 4.55 (s, 2H, $SeCH_2$)[c]; 4.62 (s, 2H, SCH_2); 7.22 (s, 10H_{arom})	338
2a	56	yellow oil	164°/19	m.p. −32 to −31 °C[2,3]	1060 (C=S); 1035 (C=S)	($CDCl_3$): 2.72 (s, 6H, $SeCH_3$)[c]	234
2b	60	yellow needles	55–57°	$C_{15}H_{14}SSe_2$ (384.3)	1040 (C=S)	(CCl_4): 4.57 (s, 4H, $SeCH_2$)[c]; 7.16 (s, 10H_{arom})	386
3a	5	red oil	89–90°/0.5	b.p. 89–90 °C/ 0.5 torr[2]; b.p. 99–100 °C/ 1 torr[3]	885 (C=Se); 860 (C=Se)	($CDCl_3$): 2.75 (s, 6H, $SeCH_3$)[c]	280
4a	80	red oil	155°/25	$C_3H_6S_2Se$ (185.2)	890 (C=Se); 845 (C=Se)	(CCl_4): 2.80 (s, 6H, SCH_3)	186
4b	33	red needles	42–44°	$C_{15}H_{14}S_2Se$ (337.4)	850 (C=Se)	($CDCl_3$): 4.53 (s, 4H, SCH_2); 7.25 (s, 10H_{arom})	338
4c	70	red needles	18–20°	$C_9H_{10}S_2Se$ (261.3)	885 (C=Se); 850 (C=Se)	(CCl_4): 2.72 (s, 3H, SCH_3); 4.57 (s, 2H, SCH_2); 7.25 (s, 5H_{arom})	262

[a] Satisfactory microanalyses obtained: C ±0.30, H ±0.20, S ±0.35.

[b] M$^+$ based on ^{80}Se isotope peak.

[c] This peak was accompanied with side-bands.

***S,Se*-Dimethyl Dithioselenocarbonate (1a); Typical Procedure:**
An aqueous sodium borohydride solution [2.27 g, 60 mmol in water (25 ml)] is added dropwise at 0 °C to a mixture of degassed water (25 ml) and selenium (2.3 g, 29 mmol)[4] under an argon atmosphere. After stirring at room temperature for 30 min, sodium hydroxide (1.3 g, 29 mmol) is added, the mixture is stirred further for 15 min, and carbon disulfide (5 ml) in tetrahydrofuran (50 ml) is added. After stirring for 3 h, methyl iodide (15 ml) is added, the stirring is continued for 3 h more, and the mixture is extracted with hexane (3 × 40 ml). Evaporation of the extract gives a red oil, which is purified by column chromatography on silica gel using hexane as eluent to give **1a** as a red oil; yield: 2.68 g (50 % based on the selenium used).

***Se,Se'*-Dimethyl Thiodiselenocarbonates (2a); Typical Procedure:**
To an oxygen-free, aqueous suspension (50 ml) containing selenium (4.6 g, 58 mmol) is added dropwise under an argon atmosphere degassed aqueous sodium borohydride [5.1 g, 135 mmol in water (50 ml)]. The mixture is stirred at room temperature for 30 min, treated with aqueous sodium hydroxide [2.32 g, 58 mmol, in water (30 ml)], and stirred for an additional 1 h. To the resulting mixture cooled in an ice bath is added dropwise thiophosgene (2.2 ml, 29 mmol) in tetrahydrofuran (40 ml) with stirring. After stirring at room temperature for 1.5 h, methyl iodide (4.4 ml, 70 mmol) is added and the mixture is stirred at room temperature for an additional 2 h. The red oil deposited is extracted with hexane (3 × 60 ml) and the extract is evaporated to give a red oil, which is purified by column chromatography on silica gel using hexane as an eluent; from the first yellow fraction **2a** is obtained as yellow oil; yield: 3.77 g (56 %, based on the selenium used) and from the second fraction, a small amount of dimethyl triselenocarbonate (**3**) is obtained as a red oil.

In the above procedure, a reverse addition of sodium hydroxide and thiophosgene to the aqueous sodium hydrogen selenide solution generated from sodium borohydride and selenium results in the formation of **2a**; yield: 2.2 g (33 %) and **3**, yield: 0.43 g (5 %).

***S*-Benzyl-*S*-Methyl-Dithioselenocarbonates (4c); Typical Procedure:**
Benzyl bromide (2.4 ml, 20 mmol) is added dropwise under ice-cooling to a stirred ammonium dithiocarbamate (2.2 g, 20 mmol) solution in acetone (15 ml) under an argon atmosphere. The mixture is stirred for 1 h at room temperature until a white precipitate appears. To the reaction mixture methyl iodide (2 ml, 32 mmol) is added and the stirring is continued at room temperature for 8 h. The white solid product is collected and washed with acetone to give a mixture of *S*-benzyl-*S*-methyl iminodithiocarbonate hydroiodide and ammonium bromide (7.6 g, 90 %). The obtained salts are dissolved in a mixture of ethanol (5 ml), water (15 ml), and hexane (15 ml). To the resulting solution hydrogen selenide[4] is bubbled with stirring until the hexane layer becomes red. The hexane layer is then separated and evaporated to leave a red oil, which is purified by short column chromatography on silica gel using hexane as eluent to give **4c** as a red oil yield: 3.7 g (70 %, based on ammonium dithiocarbamate used).

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[1] Yokoyama, M., Nakamura, M., Imamoto, T., Yamaguchi, K. *J. Chem. Soc. Chem. Commun.* **1981**, 560.
Yokoyama, M., Nakamura, M., Ohteki, H., Imamoto, T., Yamaguchi, K. *J. Org. Chem.* **1982**, *47*, 1090.
Yokoyama, M., Kodera, M., Imamoto, T. *J. Org. Chem.* **1984**, *49*, 74.

[2] Gattow, G., Dräger, M. *Z. Anorg. Allg. Chem.* **1966**, *348*, 229.
Dräger, M., Gattow, G. *Chem. Ber.* **1971**, *104*, 1429.
Dräger, M., Gattow, G. *Spectrochimica Acta* **1972**, *28 A*, 425.

[3] Henriksen, L. *Acta Chem. Scand.* **1967**, *21*, 1981.

[4] Woods, T.S., Klayman, D.L. *J. Org. Chem.* **1974**, *39*, 3716.
Klayman, D.L., Griffin, T.S. *J. Am. Chem. Soc.* **1973**, *95*, 197.