A Convenient Preparation of Aryl Arylcarbonyl Diselenides

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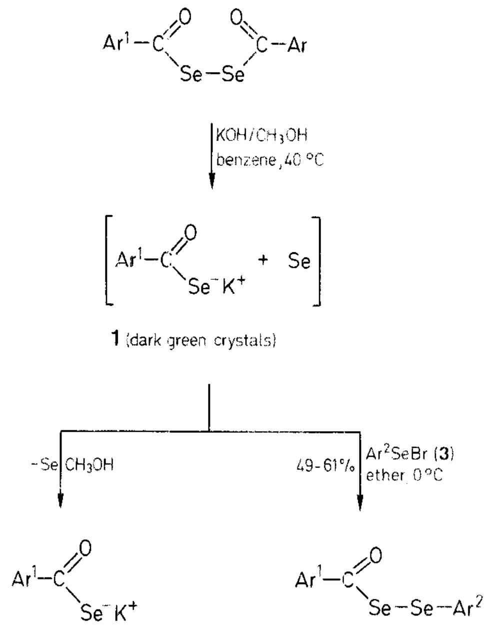
A novel method for the synthesis of aryl arylcarbonyl diselenides *via* the reaction of potassium areneselenocarboxylates with areneselenenyl bromides is described.

The chemistry of acyl alkyl disulfides [$R^1C(O)SSR^2$][1] and *s*-alkylseleno thiocarboxylates [$R^1C(O)SSeR^2$][2], which are of interest from the viewpoint of organic synthesis, biochemistry, and polymer chemistry, is well studied. In contrast, the chemistry of acyl alkyl diselenides [$R^1C(O)SeSeR^2$] has not yet been reported. In earlier work, we developed a novel method for the preparation of potassium and piperidinium selenocarboxylates.[3] As an extension of that methodology, we herein describe the preparation of aryl arylcarbonyl diselenides **4** by the reaction of the salts of areneselenocarboxylic acids with areneselenenyl bromides **3**.

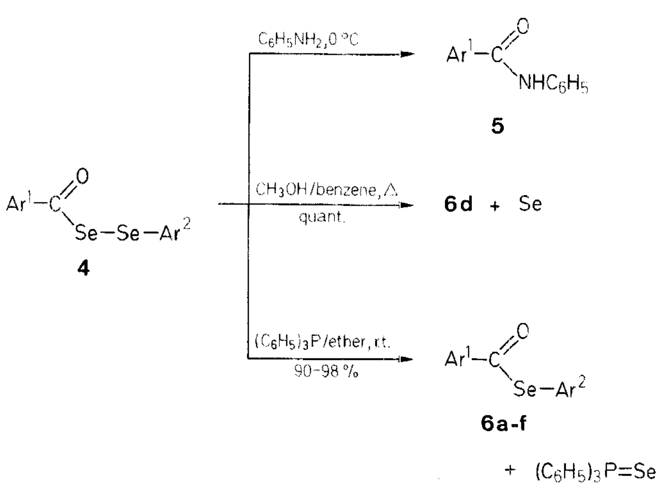


Thus, the treatment of bis(arenecarbonyl) diselenide with an equimolar amount of methanolic potassium hydroxide affords an 1 : 1 adduct of potassium areneselenocarboxylate and metal selenium as dark green crystals.[4] The reaction of the dark green crystals **1** with areneselenenyl bromide in dry ether at 0 °C affords **4** in over 50 % yield. The use of a slight excess salts **1** is required for good results. The procedures are easy, and the products can be readily recrystalized from *n*-hexane. The yields and some physical properties of the diselenides **4** obtained are summarized in Table 1.

The aryl arylcarbonyl diselenides **4** are stable in a dry atmosphere for over a month. In addition, no decomposition of **4** is observed when refluxed in benzene for 3 h. Diselenides **4** decompise, however, on silica gel chromatography.

Aryl arylcarbonyl diselenides **4** are easily reacted with aniline at 0 °C to give the corresponding amides **5**.

Interestingly, diselenides **4** are gradually deselenized in a polar solvents such as methanol to give the corresponding selenocarboxylic esters **6**.[4] Thus, the refluxing of 4-chlorobenzoyl phenyl diselenide (**4e**) in methanol/benzene (1 : 1) produces, without methanolysis, exclusively the selenoester **6d** with the precipitation of black selenium. In aqueous acetonitrile, **6d** is also produced. Moreover, the reaction of diselenides **4** with triphenylphosphine affords selenoesters **6** in excellent yields (Table 2). Presumably, the selenium atom attached to the carbonyl group would be substantially extruded by triphenylphosphine. It is known that *S*-phenylseleno thiocarboxylates [$R^1C(O)SSeR^2$] are readily desulfurized by triphenylphosphine to give the corresponding selenoesters in good yields.[2]



Potassium Selenobenzoate (2a); Typical Procedure:

To a solution of dibenzoyl diselenide (3.68 g, 10 mmol) in benzene (80 ml) is added anhydrous methanol (20 ml), and then 1 normal methanolic potassium hydroxide (10 ml, 10 mmol. After the mixture is stirred for 5 min, at ca. 40 °C, the solvents are evaporated under reduced

Table 1. Aryl Arylcarbonyl Diselenides **4** [$Ar^1C(O)SeSeAr^2$] Prepared

Product	Ar^1	Ar^2	Yield[a] (%)	m.p. (°C)	Molecular Formula[b]	IR (KBr) (cm^{-1}) $\nu_{C=O}$	IR (KBr) (cm^{-1}) ν_{C-Se}	^1H-NMR ($CDCl_3$) δ (ppm)
4a	C_6H_5	C_6H_5	55	liq.	$C_{13}H_{10}OSe_2$ (340.1)	1684	864	7.1–8.1 (m)
4b	C_6H_5	4-$CH_3C_6H_4$	58	60–62	$C_{14}H_{12}OSe_2$ (354.2)	1684	864	2.33 (s, 3H); 7.0–8.1 (m, 9H)
4c	4-$CH_3C_6H_4$	C_6H_5	50	85–86	$C_{14}H_{12}OSe_2$ (354.2)	1698	868	2.20 (s, 3H); 7.0–8.0 (m, 9H)
4d	4-$CH_3OC_6H_4$	C_6H_5	55	43–44	$C_{14}H_{12}O_2Se_2$ (370.2)	1681	878	3.87 (s, 3H); 6.9–8.0 (m, 9H)
4e	4-ClC_6H_4	C_6H_5	61	76–78	$C_{13}H_9ClOSe_2$ (374.6)	1690	868	7.2–8.0 (m)
4f	4-ClC_6H_4	4-$CH_3C_6H_4$	49	58–60	$C_{14}H_{11}ClOSe_2$ (388.6)	1688	870	2.34 (s, 3H); 7.0–8.0 (m, 8H)
4g	4-ClC_6H_4	4-ClC_6H_4	57	88–90	$C_{13}H_8Cl_2OSe_2$ (409.0)	1688	868	7.2–7.9 (m)

[a] Yield of isolated products except **4a** (contained small amounts of diphenyl diselenide).

[b] Satisfactory microanalysis obtained: C ±0.22, H ±0.06, Se ±0.61.

Table 2. *Se*-Aryl Selenocarboxylates **6** Prepared

Product	Ar^1	Ar^2	Yield[a] (%)	m.p. (°C)	Molecular Formula[b] or Lit. m.p. (°C)	IR (KBr) (cm^{-1}) $\nu_{C=O}$	ν_{C-Se}	^{1}H-NMR (CDCl$_3$) δ (ppm)
6a	C_6H_5	C_6H_5	92	36.5–37.5	37–38[5]	1685	880	7.2–8.0 (m)
6b	C_6H_5	4-$CH_3C_6H_4$	95	73.0–73.5	71–72[6]	1680	882	2.39 (s, 3H); 7.2–8.0 (m, 9H)
6c	4-$CH_3C_6H_4$	C_6H_5	90	93.5–94.5	93–94[5]	1688	885	2.39 (s, 3H); 7.2–7.9 (m, 9H)
6d	4-ClC_6H_4	C_6H_5	93	84.0–84.5	83.5–84.5[5]	1688	885	7.4–7.9 (m)
6e	4-ClC_6H_4	4-$CH_3C_6H_4$	93	95.5–96.5	$C_{14}H_{11}ClOSe$ (309.7)	1685	878	2.36 (s, 3H); 7.1–7.9 (m, 8H)
6f	4-ClC_6H_4	4-ClC_6H_4	98	129–131	$C_{13}H_8Cl_2OSe$ (330.1)	1680	882	7.2–7.9 (m)

[a] Yield of isolated products.

[b] Satisfactory microanalyses obtained: C ±0.11, H ±0.10.

pressure. *n*-Hexane (50 ml) is added, and filtration of the resulting precipitates yields 3.0 g of dark green crystals (100% as a 1 : 1 mixture of potassium selenocarboxylate and selenium). IR (KBr): $\nu = 1550$ (C=O), 880 cm^{-1} (C–Se). The dark green crystals are dissolved in dry methanol (20 ml), and the resulting black precipitates (selenium) is filtered. Benzene (30 ml) is added to the filtrate, and the resultant mixture is concentrated to ca. 5 ml. *n*-Hexane (30 ml) is added and filtration of the resulting precipitate affords chemically pure **2a** as slight yellow needles; yield: 1.8 g (81%).

IR (KBr): $\nu = 1550$ (C=O), 880 cm^{-1} (C–Se).

4-Chlorobenzoyl Phenyl Diselenide (4e); Typical Procedure:

To a suspension containing the dark green crystals of potassium 4-chloroselenobenzoate - selenium mixture (1 : 1; 1.68 g, 5.0 mmol) in anhydrous ether (20 ml) is added dropwise benzeneselenenyl bromide (0.94 g, 4.0 mmol) in anhydrous ether (10 ml) under an argon atmosphere at 0 °C. The resulting mixture is stirred for an additional 30 min at the same temperature. After the precipitate is filtered off, the solvent is removed under reduced pressure. The resulting crude product is recrystallized from *n*-hexane to give **4e**; yield: 0.91 g (61%); mp. 76–78 °C.

$C_{13}H_9OSe_2Cl$	calc.	C 41.68	H 2.42	Se 42.16
(374.6)	found	41.55	2.39	41.97

IR (KBr): $\nu = 1690$ (C=O), 868 cm^{-1} (C–Se)

^{1}H-NMR (CDCl$_3$): $\delta = 7.2$–8.0 ppm (m, H_{arom}).

MS (20 eV): *m/e* = 376 (M$^+$), 392 (($C_6H_5)_2Se_3$), 314 (($C_6H_5)_2Se_2$), 234 (($C_6H_5)_2Se$), 139 ($ClC_6H_4CO^+$)

Reaction of 4-Chlorobenzoyl Phenyl Diselenide (4e) With Aniline:

A mixture of **4e** (0.80 g, 2.14 mmol) and aniline (0.20 g, 2.15 mmol) in anhydrous benzene (30 ml) is stirred for 4 h at 0 °C in an argon atmosphere. Hydrogen selenide generation is observed. After the resulting precipitate (Se 55 mg) is filtrated off, the solvent is removed under reduced pressure. To the residue is added *n*-hexane (50 ml) and 4-chlorobenzanilide is collected as insoluble part; yield: 0.46 g (93%); m.p. 194–195 °C.

$C_{13}H_{10}OClN$	calc.	C 67.40	H 4.35
(203.5)	found	67.18	4.32

IR (KBr): $\nu = 3360$ (N–H), 1652 (C=O), 1535 cm^{-1} (N–H).

NMR (CDCl$_3$): $\delta = 7.77$ (br, 1H, NH); 7.2–8.0 ppm (m, 9 H_{arom})

A separation of the soluble part by TLC (silica gel, hexane/ether 6 : 1 as eluent) gives diphenyl diselenide; yield: 0.29 g (43%); m.p. 60–62 °C (Lit.[7] m.p. 63 °C).

Selenium Extrusion from 4-Clorobenzoyl Phenyl Diselenide (4e) in Refluxing Benzene/Methanol (1 : 1):

A solution of **4e** (330 mg, 0.88 mmol) in benzene/methanol (1 : 1, 20 ml) is refluxed for 2 h under argon atmosphere. The resulting precipitate (selenium 70 mg) is filtered off. Removal of the solvent under reduced pressure gives *Se-phenyl 4-chloroselenobenzoate* (**6d**); yield: 260 mg (100%); m.p. 84–85 °C (Lit.[5] m.p. 83.5–84.5 °C).

IR (KBr): $\nu = 1680$ (C=O), 885 (C–Se) cm^{-1}.

Selenium Extrusion from 4-Clorobenzoyl Phenyl Diselenide (4e) With Triphenylphosphine; Typical Procedure:

A mixture of **4e** (0.75 g, 2.0 mmol) and triphenylphosphine (0.53 g, 2.0 mmol) in anhydrous ether (50 ml) is stirred under an argon atmosphere at room temperature for 1 h. The ether is evaporated under reduced pressure. To the resulting crude product mixture is added *n*-hexane (20 ml), and the insoluble part (triphenylphosphine selenide: 0.68 g; mp 187–190 °C) is filtered off. Evaporation of the filtrate and recrystallization of the residue from *n*-hexane yields *Se-phenyl 4-chloroselenobenzoate* **6d** as colorless plates (Table 2).

Received: 21 November 1985
(Revised form: 29 October 1986)

(1) Field, L., Buckman, J.D. *J. Org. Chem.* **1967**, *32*, 3467.
Bohme, H., Zinner, G. *Justus Liebigs Ann. Chem.* **1954**, *585*, 142;
Bohme, H., Zinner, G. *Justus Liebigs. Ann. Chem.* **1959**, *576*, 61
Field, L., Hanley, W.S., McVeigh, I. *J. Org. Chem.* **1971**, *36*, 2735.
Kawamura, S., Horii, T., Tsurugi, J. *J. Org. Chem.* **1971**, *36*, 3677.
Field, L., Hanley, W.S. *J. Med. Chem.* **1971**, *14*, 202.
McVeigh, I., Evans, Z. *Mycopathol. Mycol. Appl.* **1968**, *35*, 313.

(2) Kato, S., Kabuto, H., Kimura, M., Ishihara, H., Murai, T. *Synthesis* **1985**, 519.

(3) Ishihara, H., Hirabayashi, Y. *Chem. Lett.* **1976**, 203.
Ishihara, H., Muto, S., Kato, S. *Synthesis* **1986**, 128.

(4) Potassium selenocarboxylates can be isolated from the dark green crystals in ca. 80% yields (see experimental).

(5) Grieco, P.A., Yokoyama, Y., Williams, E. *J. Org. Chem.* **1978**, *43*, 1283.

(6) Taboury, F. *Bull. Soc. Chim. Fr.* **1906**, *35*, 672.

(7) Sharpless, K.B., Lauer, R.F. *J. Am. Chem. Soc.* **1973**, *95*, 2697.