A Facile Synthesis of Potassium Selenocarboxylates and Their Oxidation with XeF$_2$ to Diacyl Diselenides: An X-ray Structural Analysis of Di(4-methoxybenzoyl) Diselenide

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ABSTRACT: *Several potassium selenocarboxylates were synthesized in moderate to good yields by the direct reaction of acyl chlorides with potassium selenide. The potassium salts were readily oxidized with XeF$_2$ to give diacyl diselenides in quantitative yields. The structure of di(4-methoxybenzoyl) diselenide was established by X-ray diffraction analysis. Intramolecular interactions between the carbonyl oxygen and the selenium that is connected to the opposite carbonyl group were observed.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 373–379, 1999

INTRODUCTION

Alkali metal selenocarboxylates are among the most important starting compounds for the synthesis of selenocarboxylic acid derivatives. The first alkali metal selenocarboxylates were reported in 1976 by Hirabayashi et al. [1], who synthesized five potassium selenocarboxylates by reacting diacyl selenides with potassium hydroxide in methanol [1]. Later, we succeeded in isolating aliphatic derivatives, RCOSeK (R = alkyl), by the same method using a mixed solvent of ether/hexane (1:1) [2]. These meth-

ods, however, have some disadvantages, such as the limited availability of the starting diacyl selenides and the difficulty of purification. A more convenient synthesis of the potassium salts is required. Recently, we reported the direct synthesis of lithium [3a], sodium [3b], rubidium [3c], and cesium selenocarboxylates [3c] and of sodium and potassium tellurocarboxylates [3d] by reacting acyl chlorides with the corresponding alkali metal chalcogenides.

On the other hand, several methods for synthesizing diacyl diselenides have been reported [4–9]. Although this is not yet proven, the final step in these syntheses is considered to be oxidation of the intermediate selenocarboxylic acid or its ammonium or alkali metal salts with oxidizing agents such as oxygen or iodine. Removal of the iodine that is used as an oxidizing agent is somewhat difficult. We report here a facile synthesis of potassium selenocarboxylates and diacyl diselenides together with the first X-ray structural analysis of diacyl diselenides.

RESULTS AND DISCUSSION

Potassium Selenocarboxylates. Initially, we examined the direct preparation of potassium selenocarboxylates **1** by reacting acyl chlorides with potassium selenide. The reaction conditions are shown in Scheme 1. To prevent the formation of diacyl selenide as a by-product, an excess of potassium selenide (RCOCl/K$_2$Se = 1:1.3) was required. The use of acetonitrile as the solvent has been found to be very ef-

fective for reducing the reaction time and for the purification of **1** (Scheme 1).

For example, a solution of benzoyl chloride in acetonitrile was added to an excess of potassium selenide, and the mixture was stirred at 0°C for 1 hour. The insoluble part was filtered off. Removal of the solvent in vacuo and recrystallization of the resulting residue (micro crystalline solid) gave potassium benzenecarboselenoate **1f** in a yield of 75%. Under the same conditions, the reaction with other acyl chlorides gave the corresponding potassium selenocarboxylates **1a–e, g–l** in moderate to good isolated yields. Although the low yields of the aliphatic derivatives resulted in their loss in purification procedures (recrystallization of **1a** and **1b** resulted in large loss due to their high solubility), the reactions appear to proceed quantitatively. The structures were established by IR, by ^{1}H, ^{13}C, and ^{77}Se NMR spectroscopy, and by elemental analyses.

The resulting selenium-free potassium selenocarboxylates **1** are colorless to yellow crystals. They are relatively stable thermally and toward oxygen. In particular, the aromatic derivatives appear to be much more stable than the aliphatic ones. For example, upon exposure to air for 5 hours, no appreciable change was observed in potassium 4-methylbenzenecarboselenoate **1h**. Under oxygen-free conditions in a refrigerator (ca. −17°C), the aromatic derivatives can be stored for at least one month.

The first diacyl diselenide was reported in 1932 by Szperl and Wiorogorsky, who obtained dibenzoyl diselenide as one of the products of the reaction of benzoyl chloride with hydrogen selenide in the presence of ammonium chloride [4]. Later, diacyl diselenides have been obtained by the air oxidation of selenocarboxylic acids [5,6] and diacyl selenides [5]; the I_2 oxidation of sodium [7], potassium [1], and ammonium selenocarboxylates, which are formed from acyl chlorides, Se, and CO in the presence of amine and water [8]; and by the direct reaction of acyl chlorides with sodium diselenide, which was prepared from sodium metal and selenium in liquid

ammonia [7] or from sodium hydroxide and selenium under phase transfer conditions [9]. Recently, we succeeded in isolating a series of selenocarboxylic acids [10] and observed that these acids are gradually oxidized even in the solid state. In addition, alkali metal thio- and dithiocarboxylates were found to be readily oxidized by xenon difluoride to give diacyl and di(thioacyl) disulfides [11]. This prompted us to prepare diacyl diselenides by reacting potassium salts **1** with xenon difluoride. In fact, treatment of **1** with an equimolar amount of xenon difluoride led to a quantitative yield of diacyl diselenides **2** (Scheme 2). The oxidation of 4-methylbenzenecarboselenoic acid and its lithium, sodium, rubidium, and cesium salts under the same conditions afforded **2c** in high yields (Scheme 3).

Although XeF_2 is currently expensive, this synthetic method has several advantages compared to those using other oxidizing agents: (a) the yields of diacyl diselenides are almost quantitative, (b) the reaction procedures are simple, (c) removal of the oxidizing agent is not required, (d) the reaction conditions are mild, (e) the reaction time is very short (the reactions are completed within 5 min), and (f) completion of the reactions can be readily judged by the change in the color of the reaction mixture.
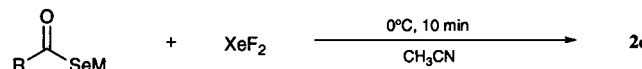
To our knowledge, no structural analysis of dia-
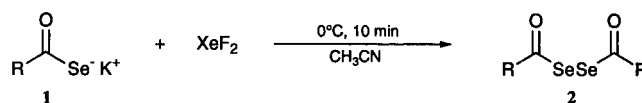
No.	R	Yield [%]
2a	C_6H_5	94
2b	$2\text{-}CH_3C_6H_4$	93
2c	$4\text{-}CH_3C_6H_4$	98
2d	$2\text{-}CH_3OC_6H_4$	91
2e	$4\text{-}CH_3OC_6H_4$	96
2f	$4\text{-}ClC_6H_4$	94
2g	$1\text{-}C_{10}H_7$	90

SCHEME 2
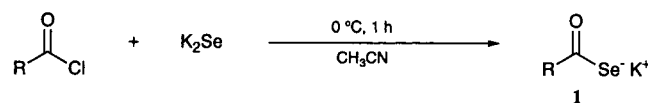
No.	R	Yield [%]	No.	R	Yield [%]
1a	CH_3	26	**1g**	$2\text{-}CH_3C_6H_4$	79
1b	C_2H_5	37	**1h**	$4\text{-}CH_3C_6H_4$	84
1c	$i\text{-}C_3H_7$	63	**1i**	$2\text{-}CH_3OC_6H_4$	62
1d	$t\text{-}C_4H_9$	62	**1j**	$4\text{-}CH_3OC_6H_4$	77
1e	$cyclo\text{-}C_6H_{11}$	64	**1k**	$4\text{-}ClC_6H_4$	78
1f	C_6H_5	75	**1l**	$1\text{-}C_{10}H_7$	72

SCHEME 1

RCOSeM		Yield of **2c** [%]
R	M	
$4\text{-}CH_3C_6H_4$	H	92^a
	Li	87
	Na	92
	K	98
	Rb	76
	Cs	74

^{a}Solvent: Et_2O

SCHEME 3

cyl diselenides has been described in the literature. After several attempts to crystallize diaroyl diselenides, we succeeded in obtaining single crystals of di(4-methoxybenzoyl) diselenide **2e**. Figure 1 shows an ORTEP drawing of the diselenide **2e**. The final atomic positional parameters are listed in Table 1. Selected bond distances and angles are shown in Table 2. The structural geometry of the diselenide **2e** essentially resembles those of dibenzoyl [12] and di(4-chlorobenzoyl) disulfides [11].

The Se11–Se21 [2.2888(9) Å] and Se11–C11 [1.986(7) Å] distances are normal, indicating single bonds. The average of the two carbonyl C–O distances is 1.197(7) Å, which is almost identical to those of common esters and thioesters. The dihedral angle (85.8°) of C11-Se11-Se21-C21 is somewhat greater than that (80.8°) of di(benzoyl) disulfide [12]. On the other hand, the dihedral angles of Se11-C11-C12-C13 and Se21-C21-C22-C23 are 177° and 165°, respectively, indicating the near planarity of the
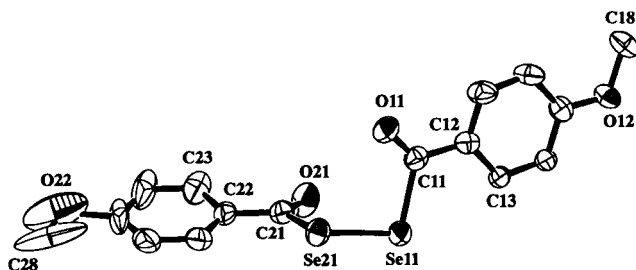

FIGURE 1   An ORTEP drawing of Di(4-methoxybenzoyl) diselenide **2e.**

TABLE 1   Crystallographic Data for Di(4-methoxybenzoyl) Diselenide **2e**

Compound	**2e**
Empirical formula	$C_{16}H_{14}O_4Se_2$
Formula weight	428.20
Crystal system	triclinic
Unit system	a = 10.3609(6) Å
	b = 12.2086(9) Å
	c = 6.991(7) Å
	α = 105.397(6) °
	β = 102.985(6) °
	γ = 102.537(6) °
Volume of unit cell (Å^3)	794.0(1)
Space group	$P\bar{1}$ (#2)
Z value	2
D_{calc} (g/cm^3)	1.791
μ(MoKα) (cm^{-1})	46.72
Temp. (°C)	−80
$2\theta_{max}$ (deg)	55.0
No. of reflections measured	total: 3936
No. of obs. [$I > 3\sigma(I)$]/variable	2061/199
Residuals: R; Rw	0.046; 0.048
Goodness-of-fit indicator	1.63

phenyl ring and the COSe group. Notably, the O11–Se21 and O21–Se11 distances are 3.184(5) and 3.162(5) Å, respectively, which are within the sum (3.40 Å) of the van der Waals radii of both atoms [13]. This clearly indicates an intramolecular interaction within both pairs of atoms. Similar interactions have been observed for the disulfides [11,12].

EXPERIMENTAL

The IR spectra were measured on a Perkin Elmer FT-IR 1640 instrument. The ^{1}H NMR spectra were recorded on a Jeol JNM-α400 (399.7 MHz) instrument with tetramethylsilane as an internal standard. ^{13}C NMR spectra were obtained by use of a Jeol JNM-α400 (100.4 MHz) spectrometer with CDCl$_3$ as an internal standard. The ^{77}Se NMR spectra were obtained by use of a Jeol JNM-α400 (76.2 MHz) instrument with dimethyl selenide as an external standard. Elemental analyses were performed by the Elemental Analysis Center of Kyoto University.

Materials. Potassium selenide [14] and 2-methyl-, 4-methyl-, 2-methoxy-, 4-methoxy-, and 4-chloro-benzoyl chlorides [15] were prepared according to the literature. Other acyl chlorides were commercial grade and distilled under N$_2$. Ether, hexane, and acetonitrile were distilled under N$_2$ from sodium benzophenone ketyl, sodium metal, and phosphorus pentoxide, respectively.

X-ray Measurements. The measurements were carried out on a Rigaku AFC7R four-circle diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). A Rigaku XR-TCS-2-050 temperature controller was used for low-temperature measurements. All of the structures were solved and refined using the teXsan crystallographic software package on an IRIS Indigo computer. The crystals of **2e** were cut from the grown needles. One of the crystals was mounted on a glass fiber. The cell dimensions were determined from a least-squares refinement of the setting diffractometer angles for 25 automatically centered reflections. Three standard reflections were measured every 150 reflections, and no decay was detected. Lorentz and polarization corrections were applied to the data, and an empirical absorption correction (ψ scan [16]) was also applied. The structure was solved by the direct method using SHELXS86 [17]. Scattering factors for neutral atoms were taken from Cromer and Waber [18], and an anomalous dispersion [19] was used. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, and the weighting scheme employed was $w = [\sigma^2(F_0) + p^2(F_0)^2/4]^{-1}$. A full-matrix least-squares refinement was executed with nonhydrogen atoms being anisotropic for **2e**.

TABLE 2 Selected Bond Lengths (Å), Angles (deg), and Torsion Angles (deg) of Di(4-methoxybenzoyl) Diselenide **2e**

<div align="center">Bond Lengths</div>

Se11-Se21	2.2888(9)	Se11-O21	3.162(5)
Se11-C11	1.986(7)	Se21-O11	3.184(5)
O11-C11	1.202(7)	Se21-C21	1.973(7)
O21-C21	1.191(7)		

<div align="center">Angles</div>

Se11-C11-O11	120.9(5)	Se21-C21-O21	121.5(6)
Se21-Se11-C11	98.3(2)	Se11-Se21-C21	97.6(2)
Se11-C11-C12	114.6(4)	Se21-C21-C22	113.5(5)
O11-C11-C12	124.5(6)	O21-C21-C22	125.0(7)

<div align="center">Torsion Angles</div>

C11-Se11-Se21-C21	85.8(3)	Se11-C11-C12-C13	177.4(5)
Se21-Se11-C11-C12	176.5(4)	Se21-C21-C22-C23	164.5(5)
Se11-Se21-C21-C22	173.2(4)		

The final least-squares cycle included fixed hydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2 times that of the connecting atoms [20].

Crystal Growth for X-ray Diffraction. Solvents: dichloromethane (1.5 mL) for 20 mg of **2e**: Hexane (2 mL) was layered on the top of a dichloromethane solution containing the diselenide **2e**. The single crystals were grown for 0.5–2 days at −20°C. One of them was mounted.

Synthesis of Potassium Selenocarboxylates (**1**)

The synthesis of potassium benzenecarboselenoate **1f** is described in detail as a typical procedures. All manipulations were performed under argon.

Potassium Selenoacetate (**1a**). Colorless microcrystals (26%); IR (Nujol): 2984, 2881, 2836, 1663, 1577 (C=O), 1470, 1455, 1378, 1346, 1120, 960, 722, 614 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ 2.54 (s, 3H, CH$_3$); ^{13}C NMR (CD$_3$OD): δ 44.6 (CH$_3$), 219.7 (C=O); ^{77}Se NMR (CD$_3$OD): δ 392.8. The IR spectrum was exactly consistent with that of the authentic sample prepared by the reaction of the corresponding diacyl selenide with potassium methanolate [2].

Potassium Ethanecarboselenoate (**1b**). Colorless microcrystals (37%); IR (Nujol): 2972, 2936, 2872, 1663, 1574, 1559 (C=O), 1460, 1441, 1409, 1366, 1310, 1241, 1122, 1050, 1013, 929, 775, 700, 583 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ 1.06 (t, J = 7.6 Hz, 3H, CH$_3$), 2.76 (q, J = 7.6 Hz, 2H, CH$_2$); ^{13}C NMR (CD$_3$OD): δ 11.4 (CH$_3$), 50.3 (CH$_2$), 224.2 (C=O); ^{77}Se NMR (CD$_3$OD): δ 356.6. The IR spectrum was exactly consistent with that of the authentic sample pre- pared by the reaction of the corresponding diacyl se- lenide with potassium methanolate [2].

Potassium 1-Methylethanecarboselenoate (**1c**). Colorless microcrystals (63%); IR (Nujol): 2962, 2868, 1575, 1558 (C=O), 1456, 1376, 1357, 1313, 1282, 1167, 1131, 1103, 1082, 965, 870, 855, 688, 572, 482 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ 1.10 (d, J = 6.8 Hz, 6H, CH$_3$), 3.02 (sept, J = 6.8 Hz, 1H, CH); ^{13}C NMR (CD$_3$OD): δ 20.8 (CH$_3$), 54.1 (CH), 228.7 (C=O); ^{77}Se NMR (CD$_3$OD): δ 336.9. The IR spectrum was exactly consistent with that of the authentic sample pre- pared by the reaction of the corresponding diacyl se- lenide with potassium methanolate [2].

Potassium 1,1-Dimethylethanecarboselenoate (**1d**). Pale yellow needles (62%); IR (Nujol): 2982, 2881, 2837, 1614, 1585, 1538 (C=O), 1471, 1455, 1380, 1358, 1261, 1203, 1094, 1036, 928, 806, 723, 610, 464 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ 1.19 (s, CH$_3$); ^{13}C NMR (CD$_3$OD): δ 29.5 (CH$_3$), 52.3 (*C*-CO), 230.3 (C=O); ^{77}Se NMR (CD$_3$OD): δ 276.7. Anal. cald for C$_5$H$_9$KOSe: C, 29.55; H, 4.46. Found: C, 29.43; H, 4.67.

Potassium Cyclohexanecarboselenoate (**1e**). Colorless microcrystalline solid (64%); IR (Nujol): 2979, 2886, 2837, 1516 (C=O), 1463, 1452, 1379, 1276, 1178, 1138, 1099, 1085, 1049, 964, 900, 880, 846, 805, 765, 697, 594, 525, 470 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ 1.25–1.94 (m, 10H, CH$_2$), 2.75 (m, 1H, CH); ^{13}C NMR (CD$_3$OD): δ 26.7, 26.9, 31.5 (CH$_2$), 64.5 (*C*HCO), 227.5 (C=O); ^{77}Se NMR (CD$_3$OD); δ 345.3. The IR spectrum was exactly consistent with that of the authentic sample prepared by the reaction of the corresponding diacyl selenide with potassium meth- anolate [2].

Potassium Benzenecarboselenoate (**1f**).   A solution of benzoyl chloride (0.316 g, 2.25 mmol) in acetonitrile solution (3 mL) was added to a suspension of sodium selenide (0.503 g, 3.20 mmol) in the same solvent (5 mL) at 0°C under an argon atmosphere. The color of the solution rapidly changed from pale yellow to yellow. The mixture was stirred at the same temperature for 1 hour. The brown precipitates (KCl, excess of K$_2$Se, and red selenium) were filtered off. The solvent from the filtrate was removed under reduced pressure. Recrystallization of the residue from a mixed solvent of acetonitrile and ether (1:1.3) in a refrigerator (ca. -17°C) gave 0.375 g (75°) of potassium benzenecarboselenoate **1f** as yellow microcrystals.

IR (Nujol): 2975, 2882, 1584, 1538 (C=O), 1456, 1377, 1301, 1261, 1200, 1162, 1074, 1022, 937, 903, 804, 767, 691, 632, 488 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ 7.28–8.15 (m, Ar); ^{13}C NMR (CD$_3$OD): δ 127.9, 128.9, 131.5, 147.1 (Ar), 216.0 (C=O); ^{77}Se NMR (CD$_3$OD): δ 364.0. Anal. calcd for C$_7$H$_5$KOSe: C, 37.67; H, 2.26. Found: C, 37.56; H, 2.11.

Potassium 2-Methylbenzenecarboselenoate (**1g**). Yellow microcrystalline solid (79%); IR (Nujol): 2984, 2882, 1606, 1557 (C=O), 1456, 1378, 1275, 1210, 1188, 1117, 1046, 944, 903, 750, 724, 674, 655, 641, 500 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ 2.37 (s, 3H, CH$_3$), 7.05–7.67 (m, 4H, Ar); ^{13}C NMR (CD$_3$OD): δ 20.1 (CH$_3$), 125.5, 127.8, 128.7, 130.9, 131.6, 151.4, (Ar), 221.1 (C=O); ^{77}Se NMR (CD$_3$OD): δ 470.8. The IR spectrum was exactly consistent with that of the authentic sample prepared by the reaction of the corresponding diacyl selenide with methanolic potassium hydroxide [1].

Potassium 4-Methylbenzenecarboselenoate (**1h**). Yellow crystals (84%); IR (Nujol): 2969, 2845, 1606, 1579, 1538 (C=O), 1456, 1377, 1295, 1198, 1162, 1108, 907, 824, 716, 629 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ 2.29 (s, 3H, CH$_3$), 7.10 (d, J = 7.8 Hz, 2H, Ar), 8.07 (d, J = 8.1 Hz, 2H, Ar); ^{13}C NMR (CD$_3$OD): δ 21.4 (CH$_3$), 128.7, 129.4, 142.1, 144.8 (Ar), 215.3 (C=O); ^{77}Se NMR (CD$_3$OD): δ 348.8. Anal. calcd for C$_8$H$_7$KOSe: C, 40.51; H, 2.97. Found: C, 39.97; H, 2.96.

Potassium 2-Methoxybenzenecarboselenoate (**1i**). Yellow microcrystals (62%); IR (Nujol): 2923, 2854, 1595, 1578, 1527, 1519 (C=O), 1484, 1436, 1302, 1276, 1259, 1183, 1160, 1120, 1054, 1015, 927, 899, 789, 737, 672, 660, 638, 582, 545, 501 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ 3.80 (s, 3H, CH$_3$O), 6.88–7.73 (m, 4H, Ar); ^{13}C NMR (CD$_3$OD): δ 56.3 (CH$_3$O), 112.6, 120.6, 130.1, 130.4, 141.2, 153.6 (Ar), 217.7 (C=O); ^{77}Se NMR (CD$_3$OD): δ 481.3. Anal. calcd for C$_8$H$_7$KO$_2$Se: C, 37.95; H, 2.79. Found: C, 38.14; H, 2.87.

Potassium 4-Methoxybenzenecarboselenoate (**1j**). Yellow microcrystals (77%); IR (Nujol): 2971, 2837, 1600, 1584, 1532 (C=O), 1500, 1454, 1260, 1200, 1154, 1106, 1016, 905, 790, 702, 628, 619, 471 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ 3.79 (s, 3H, CH$_3$O), 6.82 (d, J = 8.7 Hz, 2H, Ar), 8.20 (d, J = 8.7 Hz, 2H, Ar); ^{13}C NMR (CD$_3$OD): δ 55.9 (CH$_3$O), 113.1, 131.4, 140.1, 163.2 (Ar), 214.0 (C=O); ^{77}Se NMR (CD$_3$OD): δ 335.9. Anal. calcd for C$_8$H$_7$KO$_2$Se: C, 37.95; H, 2.79. Found: C, 37.99; H, 2.79.

Potassium 4-Chlorobenzenecarboselenoate (**1k**). Yellow microcrystals (78%); IR (Nujol): 2974, 2882, 2841, 1586, 1576, 1540 (C=O), 1458, 1377, 1261, 1195, 1156, 1104, 1086, 1010, 906, 836, 802, 720, 624, 560, 469 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ 7.29 (d, J = 8.5 Hz, 2H, Ar), 8.13 (d, J = 8.5 Hz, 2H, Ar), ^{13}C NMR (CD$_3$OD): δ 128.1, 130.7, 137.8, 140.6 (Ar), 214.0 (C=O); ^{77}Se NMR (CD$_3$OD): δ 369.7. Anal. calcd for C$_7$H$_4$ClKOSe: C, 32.63; H, 1.57. Found: C, 32.56; H, 1.69.

Potassium 1-Naphthalenecarboselenoate (**1l**). Yellow microcrystals (72%); IR (Nujol): 2972, 1564 (C=O), 1503, 1463, 1456, 1378, 1265, 1227, 1158, 1073, 1041, 1013, 901, 866, 792, 673, 624, 563 cm^{-1}; ^{1}H NMR (CD$_3$OD): δ 7.41–8.37 (m, Ar); ^{13}C NMR (CD$_3$OD): δ 125.3, 125.6, 126.4, 126.7, 126.8, 128.3, 128.5, 129.2, 134.6, 149.7 (Ar), 220.4 (C=O); ^{77}Se NMR (CD$_3$OD): δ 494.6. The IR spectrum was exactly consistent with that of the authentic sample prepared by the reaction of the corresponding diacyl selenide with methanolic potassium hydroxide [1].

Reaction of Potassium Selenocarboxylates (**1**) with Xenon Difluoride [Preparation of Diacyl Diselenide (**2**)]

Typical procedures are described in detail for the preparation of di(4-methylbenzoyl) diselenide (**2c**). The IR spectra of the diselenides **2** were exactly consistent with those of the authentic samples prepared by the oxidation of the corresponding sodium selenocarboxylates with I$_2$ [7].

Dibenzoyl Diselenide (**2a**).   Yellow microcrystals (94%); m.p.: 129–130°C (Ref. [9], 130–131°); IR (KBr): 3043, 1740 (C=O), 1694 (C=O), 1682, 1591, 1578, 1484, 1445, 1338, 1314, 1304, 1246, 1197, 1173, 1098, 1047, 1022, 997, 930, 863, 770, 687, 665,

628, 617, 490 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.48 (t, J = 7.8 Hz, 2H, Ar), 7.62 (d, J = 7.8 Hz, 1H, Ar), 7.99 (d, J = 7.8 Hz, 2H, Ar); ^{13}C NMR (CDCl$_3$): δ 128.1, 129.1, 134.4, 136.7 (Ar), 187.3 (C=O); ^{77}Se NMR (CDCl$_3$): δ 615.3.

Di(*2-methylbenzoyl*) *Diselenide* (**2b**). Yellow microcrystals (93%); m.p. 104–105°C; IR (KBr): 3011, 2976, 1735 (C=O), 1705 (C=O), 1596, 1565, 1476, 1457, 1380, 1294, 1280, 1202, 1186, 1165, 1118, 1050, 1034, 992, 947, 857, 760, 716, 660, 632, 618, 567, 485, 455 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 2.47 (s, 3H, CH$_3$), 7.24 (d, J = 7.6 Hz, 1H, Ar), 7.30 (d, J = 7.6 Hz, 1H, Ar), 7.42 (d, J = 7.6 Hz, 1H, Ar), 7.98 (d, J = 7.6 Hz, 1H, Ar); ^{13}C NMR (CDCl$_3$): δ 20.5 (CH$_3$), 126.1, 129.3, 131.7, 132.6, 136.4, 136.5 (Ar), 188.8 (C=O); ^{77}Se NMR (CDCl$_3$): δ 649.1.

Di(*4-methylbenzoyl*) *Diselenide* (**2c**). Xenon difluoride (0.124 g, 0.73 mmol) was added to a solution of potassium 4-methylbenzenecarboselenoate (0.174 g, 0.73 mmol) in acetonitrile (10 mL) at 0°C (the color of the reaction solution immediately changing from orange to pale yellow). The mixture was stirred at this temperature for 10 minutes. The solvent was evaporated under reduced pressure. The resulting residue (reddish orange) was extracted with dichloromethane (10 mL). Removal of the dichloromethane under reduced pressure gave 0.143 g (98%) of chemically pure di(4-methylbenzoyl) diselenide **2c** as yellow microcrystals: m.p.: 110–111°C (Ref. [9], 110–111.5°C); IR (KBr): 3025, 1744 (C=O), 1699 (C=O), 1648, 1600, 1571, 1500, 1448, 1405, 1381, 1307, 1197, 1168, 1120, 1016, 865, 844, 810, 778, 710, 626, 609, 460 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 2.30 (s, 3H, CH$_3$), 7.18 (d, J = 8.2 Hz, 2H, Ar), 7.80 (d, J = 8.2 Hz, 2H, Ar); ^{13}C NMR (CDCl$_3$): δ 21.8 (CH$_3$), 128.2, 129.7, 134.1, 145.4 (Ar), 186.7 (C=O); ^{77}Se NMR (CDCl$_3$): δ 608.6.

Di(*2-methoxybenzoyl*) *Diselenide* (**2d**). Yellow microcrystals (91%); m.p.: 123–125°C; IR (KBr): 3040, 2941, 2836, 1676 (C=O), 1651 (C=O), 1595, 1484, 1464, 1436, 1312, 1286, 1246, 1187, 1167, 1110, 1048, 1013, 952, 872, 791, 755, 737, 657, 627, 610, 527, 512 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 4.06 (s, 3H, CH$_3$O), 7.02 (t, J = 7.6 Hz, 1H, Ar), 7.06 (d, J = 7.6 Hz, 1H, Ar), 7.54 (t, J = 7.6 Hz, 1H, Ar), 7.86 (d, J = 7.6 Hz, 1H, Ar); ^{13}C NMR (CDCl$_3$): δ 55.8 (CH$_3$O), 112.0, 121.0, 126.3, 129.7, 135.0, 159.3 (Ar), 185.0 (C=O); ^{77}Se NMR (CDCl$_3$): δ 681.1.

Di(*4-methoxybenzoyl*) *Diselenide* (**2e**). Yellow microcrystals (96%); m.p.: 105.5–107°C (Ref. [9], 106–107°C); IR (KBr): 3040, 2971, 1728 (C=O), 1708

(C=O), 1596, 1572, 1504, 1460, 1420, 1325, 1304, 1266, 1207, 1162, 1115, 1021, 873, 840, 833, 798, 777, 647, 610, 498, 452 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 3.88 (s, 3H, CH$_3$O), 6.96 (d, J = 9.0 Hz, 2H, Ar), 7.99 (d, J = 9.0 Hz, 1H, Ar); ^{13}C NMR (CDCl$_3$): δ 55.6 (CH$_3$O), 114.3, 129.4, 130.0, 164.5 (Ar), 185.4 (C=O); ^{77}Se NMR (CDCl$_3$): δ 599.7.

Di(*4-chlorobenzoyl*) *Diselenide* (**2f**). Yellow microcrystals (94%); m.p.: 122–124°C (Ref. [9], 122–124°C); IR (KBr): 3084, 1786, 1734 (C=O), 1692 (C=O), 1654, 1582, 1570, 1560, 1508, 1482, 1397, 1294, 1198, 1169, 1087, 1010, 868, 831, 743, 719, 628, 618, 556, 465 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.40 (d, J = 8.1 Hz, 2H, Ar), 7.85 (d, J = 8.1 Hz, 2H, Ar); ^{13}C NMR (CDCl$_3$): δ 129.4, 129.5, 134.9, 141.0 (Ar), 186.6 (C=O); ^{77}Se NMR (CDCl$_3$): δ 618.6.

Di(*1-naphthoyl*) *Diselenide* (**2g**). Yellow microcrystals (90%); m.p.: 99–103°C; IR (KBr): 3035, 1693 (C=O), 1592, 1570, 1506, 1458, 1366, 1342, 1270, 1213, 1169, 1078, 1047, 924, 884, 800, 792, 770, 734, 664, 653, 604, 563, 511, 495, 486, 458 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 7.36–7.58 (m, 3H, Ar), 7.71–7.80 (m, 1H, Ar), 8.21–8.29 (m, 2H, Ar), 8.46–8.53 (m, 1H, Ar); ^{13}C NMR (CDCl$_3$): δ 124.4, 124.9, 126.9, 128.0, 128.3, 128.5, 129.1, 133.6, 134.0, 134.2 (Ar), 188.8 (C=O); ^{77}Se NMR (CDCl$_3$): δ 659.1.

Reaction of 4-Methylbenzenecarboselenoic Acid with XeF$_2$. Xenon difluoride (0.105 g, 0.62 mmol) was added to a solution of 4-methylbenzenecarboselenoic acid (0.124 g, 0.62 mmol) in ether (5 mL) at 0°C (the color immediately changing from reddish orange to pale yellow). The solvent was evaporated under reduced pressure to give 0.130 g (92%) of chemically pure di(4-methylbenzoyl) diselenide **2c.**

Reaction of Sodium 4-Methylbenzenecarboselenoate with XeF$_2$. Xenon difluoride (0.124 g, 0.74 mmol) was added to a solution of sodium 4-methylbenzenecarboselenoate (0.163 g, 0.737 mmol) in acetonitrile (10 mL) at 0°C (the color immediately changing from orange to pale yellow). The mixture was stirred at this temperature for 10 minutes. The solvent was evaporated under reduced pressure. The resulting residue (reddish orange) was extracted with dichloromethane (10 mL). Removal of the dichloromethane under reduced pressure gave 0.135 g (92%) of chemically pure di(4-methylbenzoyl) diselenide **2c.**

Reaction of Lithium 4-Methylbenzenecarboselenoate with XeF$_2$. Similarly to the sodium salt, the reaction of lithium 4-methylbenzenecarboselenoate

(0.159 g, 0.775 mmol) with XeF$_2$ (0.130 g, 0.768 mmol) gave 87% of **2c.**

Reaction of Rubidium 4-Methylbenzenecarboselenoate with XeF$_2$.   Similarly to the sodium salt, the reaction of rubidium 4-methylbenezenecarboselenoate (0.142 g, 0.501 mmol) with XeF$_2$ (0.085 g, 0.502 mmol) gave 76% of **2c.**

Reaction of Cesium 4-Methylbenzenecarboselenoate with XeF$_2$.   Similarly to the sodium salt, the reaction of cesium 4-methylbenzenecarboselenoate (0.192 g, 0.580 mmol) with XeF$_2$ (0.098 g, 0.579 mmol) gave 74% of **2c.**

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