Synthesis and Characterization of *Se*-Organoarsanyl Selenocarboxylates

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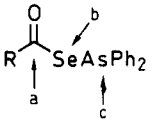
Sodium selenocarboxylates were found to react with organoarsanyl chlorides $Ph_{3-n}AsCl_n$ **1–3** (n = 1, 2, 3) to give the corresponding *Se*-organoarsanyl esters $RCOSeAsPh_2$ **(5)**, $(RCOSe)_2AsPh$ **(6)** and $(RCOSe)_3As$ **(7)** in good yields. The reaction of *Se*-diphenylarsanyl 4-methylbenzenecarboselenoate **5g** with phenylselenenyl bromide and phenyltellurenyl iodide afforded the corresponding *Se*-phenylselenenyl **13** and *Se*-phenyltellurenyl esters **14** in moderate yields, while the reaction with sodium phenoxide gave sodium 4-methylbenzenecarboselenoate **(4g)**, phenyl 4-methylbenzoate **(11)** and phenoxydiphenylarsine **(12)**, indicating the attack of phenoxy anion to both the carbonyl carbon and arsenic atoms.

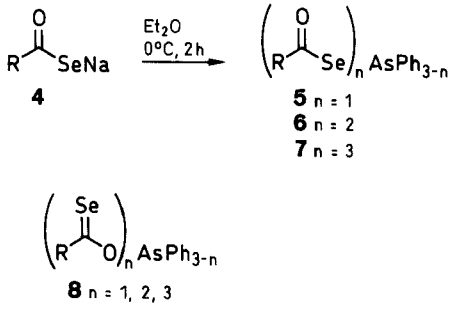
Most of the studies on selenocarboxylic acid derivatives have been limited to selenocarboxylic acid *Se*-esters because of the difficulty of synthesis.[1] Recently, we have established a convenient synthesis of sodium selenocarboxylates which are one of the most important starting compounds for the preparation of selenocarboxylic acid derivatives,[2] and have reported the synthesis of organo group 14 element esters such as $[RC(O)Se]_nER'_{4-n}$ (n = 1–4; E = Ge,[3] Sn,[4] Pb[5]) and $RC(Se)OSiR'_3$.[6] No synthetic precedent of the organo group 15 element esters such as $[RC(O)Se]_nER'_{3-n}$ (n = 1–3; E = N, P, As, Sb, Bi) has been so far reported. In this paper, we describe the preparation and characterization of *Se*-organoarsanyl selenocarboxylates $[RC(O)Se]_nAsR'_{3-n}$ [**5** (n = 1), **6** (n = 2), **7** (n = 3)].

After several attempts, sodium selenocarboxylates **4**[2] were found to react with diphenylarsanyl chloride, phenylarsanyl dichloride and trichloroarsine under the conditions shown in Scheme 1 to give the corresponding *Se*-organoarsanyl selenocarboxylates **5–7** in good yields (Table 1). In the reaction of selenocarboxylates **4** with organoarsanyl chlorides **1–3** the formation of *O*-arsanyl esters **8** was not observed spectroscopically under the reaction conditions employed. Assignment of the obtained esters **5–7** was based on IR, ^1H, ^{13}C, ^{77}Se NMR, MS spectra and micro analysis (Table 1).

The *Se*-arsanyl esters **5–7** are yellow oils or crystals and they did not decompose even on standing in air for a week. In the IR spectra, the characteristic strong absorption bands due to C=O stretching frequencies are observed in the region of 1650–1715 cm^{-1}. The ^{13}C NMR spectra show a signal at the region of δ = 190–200 for the $^{13}C{=}O$ group. The ^{77}Se resonances are observed as a singlet in the region of δ = 560–670. The mass spectra of **5** show molecular ions, while the molecular ion peaks of **6** and **7** were not detected. The fragment ions due to $RC{=}O^+$ were observed without exception as a base ion peak for **5–7**. The esters **5–7** bear the multi-reaction sites in themselves as shown with the arrows a, b, and c.

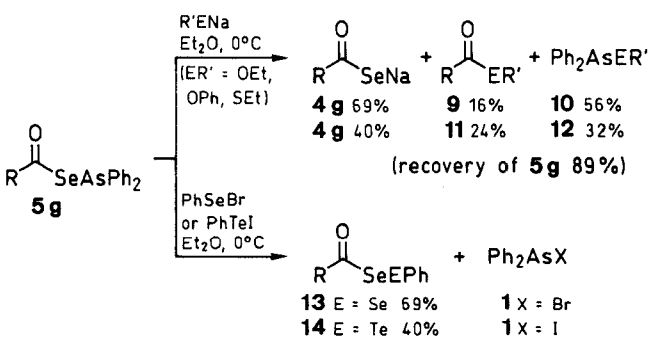


Thus, by using 4-methyl derivative **5g** as a representative *Se*-arsenyl ester, several reactions with sodium ethoxide, phenoxide, ethanethiolate, phenylselenenyl bromide and phenyltellurenyl iodide were carried out (Scheme 2). Sodium selenocarboxylate **4g** and the corresponding esters **9** and **11** along with Ph_2AsER' (**9** and **11**, ER' = OEt, OPh) were obtained, indicating that nucleophilic substitutions took place competitively on both the arsenic and the carbonyl carbon atoms. In contrast, the reaction with phenylselenenyl bromide or phenyltellurenyl iodide under the same conditions afforded the respective product



4–7	R
a	Me
b	Et
c	*i*-Pr
d	*t*-Bu
e	Ph
f	2-MeC_6H_4
g	4-MeC_6H_4
h	2-$MeOC_6H_4$
j	4-ClC_6H_4
k	3-Cl-2,6-$(MeO)_2C_6H_2$

Scheme 1



Scheme 2

Table 1. *Se*-Organoarsanyl Selenocarboxylates **5a–k**, **6a–b**, **6d–j** and **7a–b**, **7d–j** Prepared

Compound	Yield[a] (%)	mp (°C) (dec)	IR (KBr or film) $\nu_{C=O}$ (cm^{-1})	^1H NMR ($CDCl_3$/TMS) δ, J (Hz)	^{13}C NMR ($CDCl_3$/TMS) δ (C=O)	^{77}Se NMR [$CDCl_3$/Me_2Se (ext)], δ
5a	84	oil	1707	2.36 (s, 3H, CH_3), 7.21–7.49 (m, 10H)	195.1	610.7
5b	74	oil	1705	1.10 (t, J = 7.8, 3H, CH_3), 2.70 (q, J = 7.8, 2H, CH_2), 7.30–7.73 (m, 10H)	200.0	590.6
5c	70	oil	1705	1.11 (d, J = 7.3, 6H, CH_3), 2.78 (m, J = 7.3, 1H), 7.10–7.72 (m, 10H)	204.1	576.0
5d	79	oil	1711	1.21 (s, 9H, CH_3), 7.21–7.52 (m, 10H)	207.4	566.2
5e	70	124–126	1684	7.21–8.09 (m, 15H)	192.7	586.1
5f	76	121–123	1680	2.40 (s, 3H, CH_3), 7.05–7.90 (m, 14H)	194.6	624.8
5g	90	106–109	1665	2.28 (s, 3H, CH_3), 7.17–7.84 (m, 14H)	192.5	597.6
5h	82	99–101	1639	3.92 (s, 3H, CH_3O), 6.98–7.74 (m, 14H)	190.0	666.8
5i	82	72–75	1635	3.86 (s, 3H, CH_3O), 6.83–8.02 (m, 14H)	190.7	619.1
5j	80	100–104	1657	7.26–7.80 (m, 14H)	190.8	602.9
5k	88	80–82	1690	3.59 (s, 3H, CH_3O), 3.81 (s, 3H, CH_3O), 7.26–7.80 (m, 12H)	191.8	667.9
6a	63	oil	1715	2.49 (s, 6H, CH_3), 7.31–7.72 (m, 5H)	195.9	605.8
6b	77	oil	1710	1.12 (t, J = 7.8, 6H, CH_3), 2.70 (q, J = 7.8, 4H, CH_2), 7.30–7.73 (m, 5H)	200.0	584.3
6d	75	107–111	1711	1.18 (s, 18H, CH_3), 7.30–7.79 (m, 5H)	208.4	553.3
6e	70	122–125	1650	7.24–8.14 (m, 15H)	193.8	567.1
6f	69	122–124	1670	2.32 (s, 6H, CH_3), 7.03–7.80 (m, 13H)	195.0	607.1
6g	84	153–156	1645	2.32 (s, 6H, CH_3), 7.17–7.85 (m, 13H)	186.4	561.7
6h	69	119–121	1677	3.79 (s, 6H, CH_3O), 7.00–7.93 (m, 13H)	190.4	639.4
6i	84	131–134	1688	3.85 (s, 6H, CH_3O), 6.91–7.94 (m, 13H)	186.9	554.0
6j	71	142–145	1689	7.27–7.87 (m, 13H)	192.6	569.3
7a	70	oil	1718	2.56 (s, 9H, CH_3)	196.0	618.5
7b	69	oil	1720	1.23 (t, J = 7.8, 9H, CH_3), 2.89 (q, J = 7.8, 6H, CH_2)	200.5	597.9
7d	74	86–91	1710	1.41 (s, 27H, CH_3)	208.1	564.6
7e	77	125–128	1690	7.42–8.16 (m, 15H)	188.5	574.5
7f	71	99–101	1683	2.40 (s, 9H, CH_3), 7.05–7.90 (m, 12H)	194.6	612.2
7g	77	97–99	1680	2.39 (s, 9H, CH_3), 7.17–7.91 (m, 12H)	188.2	569.3
7h	67	109–111	1659	3.99 (s, 9H, CH_3O), 6.95–7.80 (m, 12H)	185.1	683.0
7i	67	96–99	1632	3.84 (s, 9H, CH_3O), 6.86–7.97 (m, 12H)	186.7	561.4
7j	60	126–131	1657	7.38–7.88 (m, 12H)	187.0	622.9

[a] Isolated yield.

13 or **14** as a main product along with the corresponding Ph_2AsX **1**. However, the reaction with sodium ethanethiolate did not occur even in prolonged reaction time over 12 hours.

In summary, we found *Se*-arsanyl esters **5–7** were synthesized from the corresponding sodium selenocarboxylates and organoarsanyl chlorides. In addition, *O*-arsanyl esters **8** were not detected spectroscopically in the reaction conditions. *Se*-Diphenylarsanyl ester **5g** was found to react with nucleophiles such as sodium ethoxide and phenoxide to give sodium selenocarboxylate **4g** and ester **9**, while the reaction with electrophiles such as phenylselenenyl bromide and phenyltellurenyl iodide afforded the corresponding *Se*-phenylselenenyl **13** and *Se*-phenyltellurenyl esters **14**, respectively.

The melting points were determined by using a Yanagimoto micro melting point apparatus (uncorrected). The IR spectra were measured on a Perkin-Elmer 1640 IR spectrophotometer. The ^1H NMR spectra were recorded on JEOL JNM-GX-270 (270 MHz) and HITACHI R-1500 (60 MHz) with TMS as an internal standard. The ^{13}C NMR (68 MHz) spectra were obtained from a JEOL JNM-GX-270. ^{77}Se NMR (52 MHz) spectra were recorded with the same apparatus as the measurement of ^{13}C NMR with Me_2Se as an external reference. The mass spectra were carried out on Shimadzu GCMS 9020-DF high resolution mass spectrometer. Elemental analyses were performed by Analytical Center of Kyoto University.

$AsCl_3$, bromobenzene, Mg turnings were commercial grade and used without further purification. NaOEt, NaOPh, and NaSEt were prepared according to the standard methods. Sodium selenocarboxylates,[2] $AsPh_3$,[7] Ph_2AsCl,[8] $PhAsCl_2$,[8] PhSeBr,[9] and PhTeI[10] were prepared according to the literature. The following solvents were purified under N_2 or Ar atmosphere and dried as indicated: hexane, Et_2O and THF were refluxed with Na metal and distilled before use; CH_2Cl_2 and MeCN were distilled over P_2O_5. EtOH was distilled over $Mg(OEt)_2$. Silica gel used on column chromatography is BW-820MH of Fuji Devision Chemical Co. Ltd. All manipulations were carried out under N_2 or Ar atmosphere. All new com-

pounds gave either satisfactory microanalyses (C ± 0.34, H ± 0.19) or HRMS values: ± 0.0014 amu. Compounds **5c,d,e, 6a,d,h–j** and **7a,d,e,j** were not analysed.

***Se*-Diphenylarsanyl 4-Methylbenzenecarboselenoate (5 g); Typical Procedure:**

To sodium 4-methylbenzenecarboselenoate (**4 g**; 0.66 g, 3.00 mmol), a solution of Ph_2AsCl (**1**; 0.79 g, 3.00 mmol) in Et_2O (20 mL) was added at 0 °C. After stirring at 20 °C for 2 h, the precipitate was filtered by using a sintered glass filter (G4 grade). The filtrate was evaporated under reduced pressure (20 °C/2 Torr), and the resulting oil was recrystallized from a mixed solvent [Et_2O/hexane, 1:3] to give chemically pure **5g** yield: 1.153 g (90 %); milky white needles; mp 106–109 °C.

IR (KBr): ν = 3050, 1665, 1643, 1598, 1477, 1437, 1200, 1172, 1156, 878, 818, 782 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.6, 127.0–144.6, 192.5.

MS (EIDI, 70 eV): m/z = 428 (M^+).

Se-Diphenylarsanyl Methanecarboselenoate (**5a**): yellow liquid.

IR (neat): ν = 3055, 1707, 1576, 1480, 1430, 1386, 1094, 1019, 994, 930, 740, 692, 579 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 36.0, 128.4–137.9, 195.1.

MS (CIDI): m/z = 353 ($M^+ + 1$).

Se-Diphenylarsanyl Ethanecarboselenoate (**5b**): yellow liquid.

IR (neat): ν = 3050, 2970, 1705, 1572, 1480, 1431, 1078, 1025, 1010, 1001, 905, 742, 697 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 19.0, 47.8, 126–138.0, 200.0.

MS: (CIDI): m/z = 367 ($M^+ + 1$).

Se-Diphenylarsanyl 1-Methylethanecarboselenoate (**5c**): yellow liquid.

IR (neat): ν = 3050, 2975, 1705, 1584, 1484, 1443, 1071, 1025, 1000, 940, 841, 740, 695 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 36.0, 128.4–137.9, 204.1.

MS (CIDI) m/z = 381 ($M^+ + 1$).

Se-Diphenylarsanyl 1,1-Dimethylethanecarboselenoate (**5d**): yellow liquid.

IR (neat): ν = 3080, 2990, 1711, 1585, 1443, 1363, 904, 794, 740, 692 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 27.3, 50.4, 128.4–138.3, 207.4.

MS (CIDI): m/z = 395 ($M^+ + 1$).

Se-Diphenylarsanyl Benzenecarboselenoate (**5e**): milky white needles; mp 124–126 °C (Et_2O/hexane, 1:4).

IR (KBr): ν = 3060, 1684, 1587, 1454, 1205, 1175, 1006, 878, 777, 705, 690, 686, 631 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 127.8–139.0, 192.7.

MS (CIDI): m/z = 338 ($M^+ - Ph + 1$).

Se-Diphenylarsanyl 2-Methylbenzenecarboselenoate (**5f**): milky white needles; mp 121–123 °C (Et_2O/hexane, 1:6).

IR (KBr): ν = 3070, 1680, 1482, 1433, 1185, 1068, 1020, 998, 875, 768, 740, 694, 668 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 20.8, 125.7–139.1, 194.6.

MS (CIDI): m/z = 429 ($M^+ + 1$).

Se-Diphenylarsanyl 2-Methoxybenzenecarboselenoate (**5h**): milky white needles; mp 99–101 °C (CH_2Cl_2/Et_2O, 3:8).

IR (KBr): ν = 1639, 1598, 1490, 1440, 1288, 1250, 1187, 1178, 1160, 1112, 1015, 886, 775, 750, 698 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 55.4, 112.1–157.9, 190.0.

MS (CIDI): m/z = 445 ($M^+ + 1$).

Se-Diphenylarsanyl 4-Methoxybenzenecarboselenoate (**5i**): milky white needles; mp 72–75 °C (CH_2Cl_2/Et_2O, 3:10).

IR (KBr): ν = 3050, 1635, 1595, 1505, 1320, 1304, 1265, 1212, 1180, 1060, 1020, 888, 828, 788, 745, 695, 620 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 55.3, 113.7–163.9, 190.7.

MS (CIDI): m/z = 368 ($M^+ - Ph + 1$).

Se-Diphenylarsanyl 4-Chlorobenzenecarboselenoate (**5j**): milky white needles; mp 100–104 °C (Et_2O/hexane, 3:2).

IR (KBr): ν = 1657, 1587, 1522, 1486, 1434, 1400, 1150, 1116, 1089, 881, 826, 739, 696 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 128.6–140.1, 190.8.

MS (CIDI): m/z = 373 ($M^+ - Ph + 1$).

Se-Diphenylarsanyl 3-Chloro-2,6-dimethoxybenzenecarboselenoate (**5k**): milky white needles; mp 80–82 °C (Et_2O/hexane, 5:1).

IR (KBr): ν = 3020, 2890, 1690, 1587, 1477, 1435, 1408, 1289, 1249, 1102, 1092, 930, 902, 806, 786, 749, 700, 636 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 56.0, 62.0, 108.0–154.3, 191.8.

***Se*-Phenylarsanyl Bis(4-methylbenzenecarboselenoate) (6 g); Typical Procedure:**

To sodium 4-methylbenzenecarboselenoate (**4 g**; 0.88 g, 4.00 mmol), $PhAsCl_2$ (**2**; 0.45 g, 2.00 mmol) was added at 0 °C. After stirring at 20 °C for 2 h, the insoluble materials were filtered by using a sintered glass filter (G4 grade). The filtrate was concentrated under reduced pressure (20 °C/2 Torr), the residue purified by recrystallization from a mixed solvent [CH_2Cl_2/hexane, 1:1] to give **6g** yield: 0.92 g (84 %); pale yellow needles; mp 153–156 °C.

IR (KBr): ν = 1645, 1604, 1204, 1167, 875, 810, 783, 745, 687, 619, 608 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.5, 128.0–145.3, 186.4.

MS (CIDI): m/z = 474 ($M^+ - Ph + 1$).

Se-Phenylarsanyl Bis(methanecarboselenoate) (**6a**): yellow liquid.

IR (neat): ν = 3015, 1715, 1588, 1540, 1353, 1095, 999, 935, 740, 690, 560 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 36.1, 128.8–133.0, 195.9.

MS (CIDI): m/z = 399 ($M^+ + 1$).

Se-Phenylarsanyl Bis(ethanecarboselenoate) (**6b**): yellow liquid.

IR (neat): ν = 3070, 2960, 1710, 1482, 1435, 1112, 1075, 1007, 902, 740, 691, 540 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 9.4, 42.8, 128.6–136.7, 200.0.

MS (EIDI, 70 eV) m/z = 426 (M^+).

Se-Phenylarsanyl Bis(1,1-dimethylethanecarboselenoate) (**6d**): yellow needles; mp 107–111 °C (CH_2Cl_2/hexane, 1:1).

IR (KBr): ν = 3000, 1711, 1683, 1475, 1461, 1435, 1318, 1036, 907, 800, 748, 695, 600 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 27.3, 50.4, 128.6–137.2, 208.4.

MS (CIDI): m/z = 482 ($M^+ + 1$).

Se-Phenylarsanyl Bis(benzenecarboselenoate) (**6e**): milky white needles; mp 122–125 °C (Et_2O/hexane, 1:1).

IR (KBr): ν = 3080, 1650, 1595, 1580, 1449, 1435, 1202, 1170, 1070, 998, 876, 772, 741, 672, 627 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 127.1–138.6, 193.8.

MS (CIDI): m/z = 446 (M – Ph + 1).

Se-Phenylarsanyl Bis(2-methylbenzenecarboselenoate) (**6f**): pale yellow needles; mp 122–124 °C (Et_2O/hexane, 1:2).

IR (KBr): ν = 3070, 1670, 1641, 1600, 1561, 1470, 1455, 1327, 1294, 1230, 1185, 1120, 1071, 871, 765, 742, 712, 690, 627 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 20.9, 125.9–138.5, 195.0.

MS (CIDI) m/z = 474 ($M^+ - Ph + 1$).

Se-Phenylarsanyl Bis(2-methoxybenzenecarboselenoate) (**6h**): pale white needles; mp 119–121 °C (CH_2Cl_2/hexane, 1:1).

IR (KBr): ν = 3000, 1677, 1651, 1595, 1488, 1464, 1452, 1435, 1285, 1246, 1186, 1165, 1109, 1010, 870, 760, 655 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 55.4, 111.9–158.9, 190.4.

MS (CIDI) m/z = 506 (M+ – Ph + 1).

Se-Phenylarsanyl Bis(4-methoxybenzenecarboselenoate) (**6i**): pale white needles; mp 131–134 °C (Et_2O/hexane, 2:1).

IR (KBr): ν = 3020, 1688, 1607, 1580, 1520, 1430, 1308, 1264, 1182, 1070, 1030, 850, 782, 617 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 55.6, 113.7–164.6, 186.9.

MS (CIDI): m/z = 506 (M^+ − Ph + 1).

Se-Phenylarsanyl Bis(4-chlorobenzenecarboselenoate) **(6j)**: pale white needles; mp 142–145 °C (CH_2Cl_2/hexane, 1:2).

IR (KBr): ν = 3060, 1689, 1595, 1429, 1324, 1288, 1180, 1093, 1019, 854, 769, 749, 698 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 128.7–141.0, 192.6.

MS (CIDI) m/z = 515 (M^+ − Ph + 1).

Se-Arsanyl Tris(4-methylbenzenecarboselenoate) (7g); Typical Procedure:

$PhAsCl_3$ (**3**; 0.388 g, 1.50 mmol) was directly added into an ethereal solution (12 mL) of sodium 4-methylbenzenecarboselenoate (**4g**, 0.99 g, 4.50 mmol) at 0 °C. After stirring for 2 h at 20 °C, the insoluble solids were filtered by using a sintered glass filter (G4 grade), followed by removal of the solvent under reduced pressure (20 °C/2.0 Torr). The residue was recrystallized from a mixed solvent [Et_2O/hexane, 3:1] to give **7 g**; yield: 0.776 g (77 %); pale yellow needles; mp 97–99 °C.

IR (KBr): ν = 3060, 1680, 1652, 1604, 1230, 1167, 880, 870, 784, 620, 610 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 21.7, 124.8, 129.4, 135.6, 145.2, 188.2.

Se-Arsanyl Tris(methanecarboselenoate) **(7a)**: yellow liquid.
IR (neat): ν = 2995, 1718, 1410, 1350, 1092, 936, 565 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 35.9, 196.0.

MS (CIDI): m/z = 455 (M+ + 1).

Se-Arsanyl Tris(ethanecarboselenoate) **(7b)**: yellow liquid.
IR (neat): ν = 3060, 3010, 1720, 1465, 1415, 1385, 1120, 1085, 1015, 910, 692, 555 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 9.4, 39.4, 200.5.

MS (EIDI, 20 eV): m/z = 486 (M+).

Se-Arsanyl Tris(1,1-dimethylethanecarboselenoate) **(7d)**: milky while needles; mp 86–91 °C (Et_2O/hexane, 1:3).

IR (KBr): ν = 2990, 1710, 1665, 1473, 1461, 1440, 1390, 1365, 1226, 1030, 908, 797, 595 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 26.3, 50.9, 208.1.

Se-Arsanyl Tris(benzenecarboselenoate) **(7e)**: pale yellow needles; mp 125–128 °C (Et_2O/hexane, 1:2).

IR (KBr): ν = 3090, 1690, 1600, 1585, 1457, 1328, 1294, 1200, 1173, 934, 867, 775, 714, 689, 670 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 128.1–135.4, 188.5.

Se-Arsanyl Tris(2-methylbenzenecarboselenoate) **(7f)**: pale yellow needles; mp 99–101 °C (Et_2O/hexane, 1:2).

IR (KBr) 3030, 1683, 1541, 1455, 1426, 1356, 1256, 1180, 1154, 1100, 870, 800, 773, 720, 674, 630 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 20.8, 125.7–139.1, 194.6.

Se-Arsanyl Tris(2-methoxybenzenecarboselenoate) **(7h)**: pale yellow needles; mp 109–111 °C (CH_2Cl_2/hexane, 1:3).

IR (KBr): ν = 3050, 1659, 1604, 1587, 1493, 1472, 1462, 1442, 1288, 1248, 1189, 1165, 1110, 866, 757, 652 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 55.8, 112.1, 121.0, 129.8, 135.0, 159.4, 185.1.

Se-Arsanyl Tris(4-methoxybenzenecarboselenoate) **(7i)**: pale yellow needles; mp 96–99 °C (CH_2Cl_2/hexane, 1:3).

IR (KBr): ν = 3070, 1632, 1430, 1375, 1275, 1261, 1185, 1112, 1025, 1001, 874, 828, 743, 697 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 55.5, 114.0, 130.4, 130.9, 164.5, 186.7.

Se-Arsanyl Tris(4-chlorobenzenecarboselenoate) **(7j)**: pale yellow needles; mp 126–131 °C (Et_2O/hexane, 3:1).

IR (KBr): ν = 1657, 1588, 1400, 1201, 1120, 1090, 1010, 880, 830, 727, 611, 554 cm^{-1}.

^{13}C NMR (68 MHz, $CDCl_3$): δ = 129.3–141.3, 187.0.

Reaction of *Se*-Diphenylarsanyl 4-Methylbenzenecarboselenoate (5 g) with NaOEt:

To a solution of **5 g** (0.535 g, 1.25 mmol) in Et_2O, was added NaOEt (0.085 g, 1.25 mmol) at 0 °C and the mixture was stirred for 1 h and yellow solid precipitated. Filtration of the precipitate by using a sintered glass filter (grade G4) yielded 0.190 g of (69 %) of **4 g** as yellow microfine crystals. After removal of the solvent under reduced pressure (20 °C/2.0 Torr), the residue (yellow oil) was separated by silica gel column chromatography [Et_2O/hexane, 1:4] to give ethyl 4-methylbenzoate **(9)** (0.033 g, 16 %) as the first eluent and ethoxydiphenylarsine **(10)**[11] (0.192 g, 56 %) as the second eluent.

Reaction of *Se*-Diphenylarsanyl 4-Methylbenzenecarboselenoate (5 g) with PhONa:

To an etheral solution of **5 g** (0.480 g, 1.12 mmol), NaOPh (0.130 g, 1.12 mmol) was added at 0 °C. The mixture was stirred at 0 °C for 1 h and yellow solid precipitated. Filtration of the precipitate by using a sintered glass filter (grade G4) gave 0.092 g (40 %) of **4 g** as yellow microfine crystals. After removal of the solvent in vacuo (20 °C/2.0 Torr), column chromatography of the residue on silica gel column (Et_2O/hexane, 1:4) yielded phenyl 4-methylbenzoate **(11)** (0.056 g, 24 %) as the first eluent and phenoxydiphenylarsine **(12)**[12] (0.115 g, 32 %) as the second eluent.

Reaction of *Se*-Diphenylarsanyl 4-Methylbenzenecarboselenoate (5 g) with EtSNa:

NaSEt (0.131 g, 1.56 mmol) was added at 0 °C to an etheral solution of **5 g** (0.666 g, 1.56 mmol). The mixture was stirred for 12 h at the same temperature. Filtration of the mixture using a sintered glass filter (grade G4) resulted in the recovery of 0.116 g (89 %) of NaEtS. Upon evaporation of the filtrate under reduced pressure (20 °C/2.0 Torr), **5 g** (0.590 g) was recovered in 89 % yield.

Reaction of *Se*-Diphenylarsanyl 4-Methylbenzenecarboselenoate (5 g) with PhSeBr:

Se-Diphenylarsanyl 4-methylbenzenecarboselenoate **5g** (0.350 g, 0.82 mmol) was taken in a 20 mL round bottom flask and a solution of PhSeBr (0.193 g, 0.82 mmol) in hexane (20 mL) was added at 25 °C. The mixture was stirred at 25 °C for 0.5 h. The resulting mixture was concentrated to ca. 5 mL under reduced pressure (25 °C/2.0 Torr) and cooled to − 20 °C for 12 h. Filtration of the resulting crystals gave 4-methylbenzoyl phenyl diselenide **(13)** as yellow crystals; yield: 0.209 g (72 %).

13: mp 82–85 °C (Lit.[4] mp 85–86 °C) IR (KBr): ν = 1698 cm^{-1} (C=O). The IR spectrum was exactly consistent with that of authentic sample prepared from the reaction of *Se*-triphenylstannyl 4-methylbenzenecarboselenoate with PhSeBr.[4]

Reaction of *Se*-Diphenylarsanyl 4-Methylbenzenecarboselenoate (5 g) with PhTeI:

To a THF solution (15 mL) of **5g** (0.189 g, 0.44 mmol) was added a solution of PhTeI (0.141 g, 0.44 mol) in the same solvent (5 mL) at 20 °C and the mixture was stirred for 3 h. Removal of the solvent under reduced pressure (20 °C/2.0 Torr) gave a dark red oil. To the oil were added CH_2Cl_2 (2 mL) and hexane (8 mL), then the mixture was cooled at − 20 °C for 24 h. Filtration of the resulting orange crystals afforded 4-methylbenzoyl benzenetellurenyl selenide **(14)** as orange crystals; yield: 0.105 g (54 %).

14: mp 119–123 °C.

IR (KBr): ν = 1680 cm^{-1} (C=O).

^{1}H NMR ($CDCl_3$, 270 MHz): δ = 2.39 (s, 3 H, CH_3), 7.19–7.90 (m, 9 H, Ar).

MS (EIDI, 70 eV): m/z = 406 (M^+).

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