A Convenient Preparation of Piperidinium Selenocarboxylates

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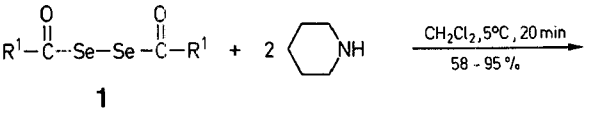
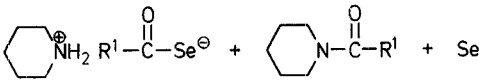
Piperidinium selenocarboxylates were isolated from the reaction of bis[acyl] diselenides with piperidine in high yields.

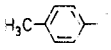
It is well known that the ammonium and alkali metal salts of thio- and dithiocarboxylic acids are easily obtained by the reaction of the corresponding acid with metal acetates or halides[1]. Selenocarboxylic acid salts cannot be prepared by a similar method because of the extreme instability of selenocarboxylic acids[2]. The only hitherto known potassium salts[3], therefore, have been prepared by treatment of thermally labile bis[acyl] selenides[4] with potassium hydroxide. In earlier work, ammonium dithiocarboxylates were found to be isolated from the reaction of bis[thioacyl] disulfides with primary and secondary amines[5]. We now report a convenient preparation of piperidinium selenocarboxylates **2** from the reaction of thermally stable bis[acyl] diselenides **1** with piperidine (Table 1).

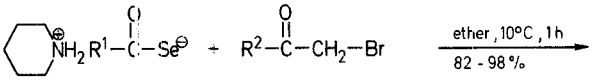


1

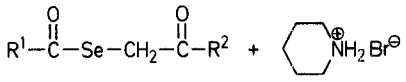


2a-g

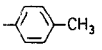
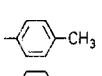
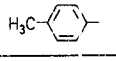
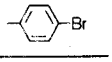
2	R¹	2	R¹
a		d	
b		e	
c		f	
		g	



2



3a-h

3	R¹	R²	3	R¹	R²
a			e		
b			f		
c			g		
d			h		

As shown in Table 1, the yields are high except for the aliphatic derivative **2g** which is less crystallizable. The aromatic salts **2a–f** are stable at 0 °C for a month, whereas the aliphatic salt **2g** completely decomposes under similar conditions within a week, but can be stored at − 20 °C over two weeks. The salts **2** dissolve in common protic and aprotic solvents and readily react with alkylating agents such as phenacyl bromide to give the corresponding esters **3** in almost quantitative yields (Table 2).

Piperidinium 4-Methoxyselenobenzoate (2d); Typical Procedure:
To a solution of bis[4-methoxybenzoyl] diselenide[4] (**1d**; 2.14 g, 5 mmol) in dichloromethane (20 ml) is added piperidine (0.85 g, 10 mmol) in the same solvent (2 ml) at 5 °C and the mixture is stirred for 20 min at 5 °C (the colour of the solution changes from reddish orange to dark green). After filtration of the precipitate (selenium metal), the solvent is then evaporated under reduced pressure. To the

Table 1. Piperidinium Selenocarboxylates **2** prepared

Product	Yield[a] [%]	m.p.[b] [°C]	Molecular Formula[c]	I.R. (KBr) $\nu_{C=O}$	[cm^{-1}] ν_{C-Se}	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS) $\delta_{C=O}$ [ppm]
2a	86	80–82°	$C_{12}H_{17}NOSe$ (270.2)	1515	906	1.5–3.4 (m, 10H); 7.1–7.9 (m, 4H); 8.9 (br. s, 2H)	216.1
2b	95	94–96°	$C_{13}H_{19}NOSe$ (284.2)	1515	906	1.5–3.2 (m, 10H); 2.32 (s, 3H); 7.1–7.9 (m, 10H); 2.32 (s, 3H)	215.2
2c	88	83–85°	$C_{13}H_{19}NOSe$ (284.2)	1500	902	1.5–3.4 (m, 10H); 2.35 (s, 3H); 7.1–8.2 (m, 4H); 8.9 (br. s, 2H)	219.8
2d	90	78–80°	$C_{13}H_{19}NO_2Se$ (300.3)	see experimental section			
2e	72	93–94°	$C_{12}H_{16}ClNOSe$ (304.7)	1560	906	1.5–3.4 (m, 10H); 7.1–7.8 (m, 4H); 8.7 (br. s, 2H)	217.5
2f	91	80–83°	$C_{12}H_{16}ClNOSe$ (304.7)	1505	900	1.5–3.4 (m, 10H); 7.2–8.3 (m, 4H); 8.9 (br. s, 2H)	214.6
2g	58	66–69°	$C_{23}H_{47}NOSe$ (432.6)	1580	945	0.88 (t, 3H); 1.25 (m, 30H); 1.5–3.4 (m, 12H); 8.2 (br. s, 2H)	222.1

[a] Yield of isolated products.
[b] Decomposition.
[c] Satisfactory microanalysis obtained: C ±0.38, H ±0.17, N ±0.04.

Table 2. *Se*-Acylmethyl Selenocarboxylates **3** prepared

Product	Yield[a] [%]	m.p. [°C]	Molecular Formula[b] or Lit. m.p. [°C]	I.R. (KBr) $\nu_{C=O}$	[cm^{-1}] ν_{C-Se}	^{1}H-N.M.R. ($CDCl_3$/TMS) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$/TMS) [ppm] δ_{COSe}	$\delta_{C=O}$
3a	92	61–62°	61.5–62°[6]	1680, 1688	894	4.43 (s, 2H); 7.1–8.1 (m, 10H)	–	–
3b	95	112–113°	$C_{15}H_{11}BrO_2Se$ (382.1)	1675, 1655	891	4.47 (s, 2H); 7.4–8.0 (m, 9H)	192.4	194.2
3c	88	60–61°	$C_{16}H_{14}O_2Se$ (317.2)	1683, 1650	883	2.48 (s, 3H); 4.49 (s, 2H); 7.2–8.1 (m, 9H)	194.5	195.4
3d	92	73–74°	$C_{16}H_{14}O_2Se$ (317.2)	see experimental section				
3e	82	96–98°	$C_{17}H_{16}O_3Se$ (347.3)	1658	890	2.39 (s, 3H); 3.84 (s, 3H); 4.48 (s, 2H); 6.8–8.0 (m, 8H)	190.7	195.1
3f	94	49–50°	$C_{15}H_{11}ClO_2Se$ (337.7)	1686, 1671	883	4.55 (s, 2H); 7.2–8.1 (m, 9H)	192.4	194.9
3g	83	98–99°	$C_{16}H_{13}ClO_2Se$ (351.7)	1667	890	2.40 (s, 3H); 4.51 (s, 2H); 7.2–8.0 (m, 8H)	191.8	194.5
3h	98	144–146°	$C_{15}H_{10}BrClO_2Se$ (416.6)	1667	884	4.48 (s, 2H); 7.4–8.0 (m, 8H)	191.5	194.1

[a] Yield of isolated product.
[b] Satisfactory microanalyses obtained: C ±0.50, H ±0.13 except for **3b** (C ±0.56, H ±0.05).

residue is added ether (20 ml) and then *n*-hexane (30 ml), and filtration of the resulting precipitate affords **2d** as bright yellow plates; yield: 1.34 g (90%); m.p. 78–80 °C (dec).

$C_{13}H_{19}NO_2Se$ (300.3) calc. C 52.00 H 6.38 N 4.66
found 51.78 6.40 4.70

I.R. (KBr): ν = 1500 (C=O); 900 cm^{-1} (C—Se).

^{1}H-N.M.R. ($CDCl_3$): δ = 1.4–3.4 (m, 10H); 4.85 (s, 3H); 6.8–8.4 (m, 4H); 8.9 ppm (br. s, 2H).

^{13}C-N.M.R. ($CDCl_3$): δ = 213.9 ppm (C=O).

***Se*-Benzoylmethyl 4-Methylselenobenzoate (3d); Typical Procedure:** Phenacyl bromide (0.70 g, 3.5 mmol) in ether (5 ml) is added to a suspension of piperidinium 4-methylselenobenzoate (**2c**, 1.00 g, 3.5 mmol) in the same solvent (30 ml) and the mixture is stirred at 10 °C for 1 h. After removal of the precipitate (piperidinium bromide) by filtration, the filtrate is washed with water (3 × 10 ml) and dried with anhydrous sodium sulfate. Evaporation of the solvent and then recrystallization of the residue from *n*-hexane (20 ml) give **3d** as colourless plates: yield: 1.02 g (92%); m.p. 73–74 °C.

$C_{16}H_{14}O_2Se$ (317.3) calc. C 60.59 H 4.45
found 60.55 4.32

I.R. (KBr): ν = 1680, 1653 (C=O), 888 cm^{-1} (C—Se).

^{1}H-N.M.R. ($CDCl_3$): δ = 2.39 (s, 3H); 4.52 (s, 2H); 7.2–8.1 ppm (m, 9H).

^{13}C-N.M.R. ($CDCl_3$): δ = 192.1 (COSe); 195.4 ppm (C=O).

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