

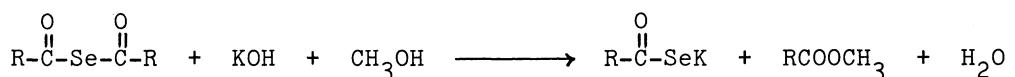
THE SYNTHESES OF POTASSIUM SELENOCARBOXYLATES AND THEIR DERIVATIVES

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Potassium selenocarboxylates were prepared in good yields on the reaction of diacyl selenides with methanolic potassium hydroxide. They were fairly stable under nitrogen and useful as starting material for the preparation of selenocarboxylic acid derivatives; methyl selenobenzoate, α -(selenobenzoyl)acetophenone, phenyl p-chlorobenzoyl diselenide, O-trimethylsilyl selenobenzoate, bis(selenostearoyl)methane, and dibenzoyl diselenide.

Metal carboxylates and thiocarboxylates have been described in many reports. On the other hand, metal selenocarboxylates which are important as starting material for the preparation of selenocarboxylic acid derivatives have been unknown so far.¹⁾ In the present study, it was found that potassium selenocarboxylates were prepared in good yields on the reaction of diacyl selenides with an equimolar amount of methanolic potassium hydroxide and they easily reacted with electrophiles to give the corresponding derivatives.



The typical procedure is described for the synthesis of potassium selenobenzoate: To a solution of dibenzoyl selenide(10.0g, 35mmol) in 80 ml of benzene was added 20 ml of methanol. Then an equimolar amount of methanolic potassium hydroxide(1N, 35mmol) was added to the solution. After the mixture was stirred for 10 minutes at 40 - 50°C, the solvents were removed under reduced pressure. To the residue was added about 30 ml of benzene and the resulting potassium selenobenzoate(la) was collected by the filtration, yield 7.3g, 95%. More purified potassium selenobenzoate was obtained on recrystallization from methanol-hexane.

The structure of la was identified by elemental analysis and studies of spectral data. Thus, in the ir spectrum(KBr disk), a very intensive absorption band due to $\text{Se}=\text{O}$ was observed at 1538 cm^{-1} . It is seen that symmetric carbonyl stretching absorption at near 1400 cm^{-1} in potassium benzoate was missing as well as thiobenzoate,²⁾ as, of course, it should be. In the uv spectrum(ethanol) maximum absorptions at 231 nm ($\log \epsilon=4.19$) and 325 nm($\log \epsilon=3.16$) were observed.

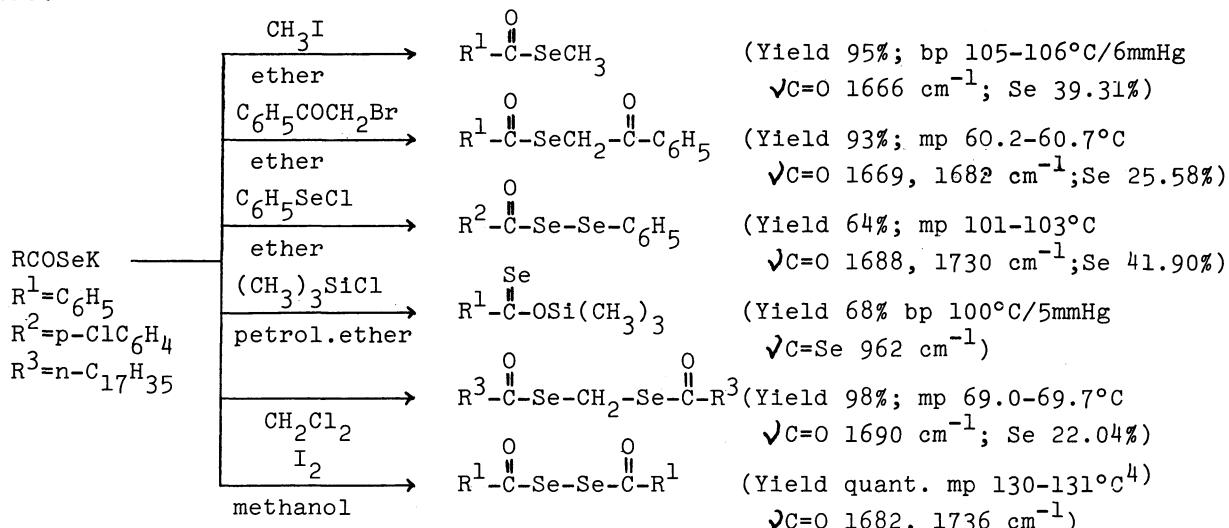
In a similar manner, various potassium selenocarboxylates were prepared in good yields on the reaction of diacyl selenides with methanolic potassium hydroxide as listed in following Table.

Table. Syntheses of Potassium Selenocarboxylates from Diacyl Selenides

Compd.	$\text{RC}\overset{\text{O}}{\underset{\text{SeK}}{\text{C}}}\text{R}$	Yield %	IR (KBr) $\nu\text{C=O, cm}^{-1}$	UV (EtOH) max(log ϵ), nm	Elemental Analysis Found(Calcd.), %		
					C	H	Se
<u>1a</u>	C_6H_5	95	1538	231(4.19) 325(3.61)	37.53 (37.67)	2.21 (2.26)	35.12 (35.38)
<u>1b</u>	$\text{p-CH}_3\text{C}_6\text{H}_4$	90	1539	240(4.17) 324(3.65)	41.86 (42.29)	3.11 (3.11)	33.06 (33.33)
<u>1c</u>	$\text{p-ClC}_6\text{H}_4$	95	1529	239(4.22) 333(3.63)	32.33 (32.64)	1.60 (1.56)	30.51 (30.68)
<u>1d</u>	$\text{p-CH}_3\text{OC}_6\text{H}_4$	88	1540	259(4.11) 319(3.79)	37.61 (37.95)	2.70 (2.79)	30.88 (31.18)
<u>1e</u>	$\text{n-C}_{17}\text{H}_{35}$	94	1560	274(3.70)	56.46 (56.08)	9.02 (9.15)	20.57 (20.49)

All the obtained potassium salts were fairly stable at room temperature under nitrogen, and did not change when left standing for a month. But the salts gradually decomposed in the air with deposition of elementary selenium.

As shown scheme, potassium selenobenzoate readily reacted with methyl iodide, α -bromoacetophenone, benzeneselenenyl chloride, and trimethylsilyl chloride at room temperature to give methyl selenobenzoate, α -(selenobenzoyl)acetophenone, phenyl p -chlorobenzoyl diselenide, and O-trimethylsilyl selenobenzoate³⁾ in 95, 93, 64, and 68% yields, respectively. Then, potassium selenostearate was stirred in dichloromethane at 40°C to give bis(selenostearoyl)methane in a 98% yield. Finally, potassium selenobenzoate was oxidized by iodine to give dibenzoyl diselenide in a quantitative yield.



References and Note

- Recently, selenobenzoic acid(PhCO-SeH) was prepared by K.A.Jensen et al. as a very unstable oil. Cf. Acta Chem.Scand., 26, 1465(1972).
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