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The Synthesis and Properties of Diacyl Selenides

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Diacyl selenides were synthesized in good yields by the deselenization of diacyl diselenides, which have conveniently been prepared from acyl chlorides and sodium hydroselenide. The reaction of dibenzoyl selenide with piperidine at 0 °C formed a fairly stable piperidinium salt. The methanolysis of distearoyl selenide gave selenostearic acid as an unstable intermediate.

Although the reactions of diacyl sulfides with various reagents have been investigated extensively, few studies of diacyl selenides have been known. In 1932, dibenzoyl selenide was obtained by Szperl and Wiorogoski[1] by the treatment of benzoyl chloride with dry hydrogen selenide in the presence of aluminium chloride. Recently, Jensen *et al.*[2] prepared dipropionyl selenide, not selenopropionic acid, by the reaction of propionyl chloride with hydrogen selenide in the presence of an equimolar amount of pyridine, but the yield was poor. In this paper, we will describe a convenient method for synthesizing diacyl selenides, which are important as the starting material for preparations of potassium selenocarboxylates,[3] by the deselenization of diacyl diselenides with triphenylphosphine and will discuss the reactions of diacyl selenides with amines and methanol.

Results and Discussion

The reaction sequence used in the synthesis of diacyl selenides is outlined in Scheme 1.

$$\mathrm{RCOCl} \xrightarrow{\mathrm{NaHSe}} [\mathrm{RCOSeH} \xrightarrow{\mathrm{NaHSe}} \mathrm{RCOSeNa}]$$

$$\Big\downarrow{\scriptstyle O_2 \text{ and } I_2}$$

$$\mathrm{RCOSeSeCOR}\ \ (\mathbf{2})$$

$$\Big\downarrow{\scriptstyle Ph_3P}$$

$$\mathrm{RCOSeCOR}\ \ (\mathbf{1})$$

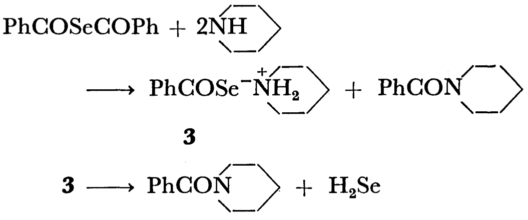
$R = C_6H_5$- (**a**), p-$CH_3C_6H_4$- (**b**), p-ClC_6H_4- (**c**), p-$CH_3OC_6H_4$- (**d**), n-$C_{17}H_{35}$- (**e**).

Scheme 1.

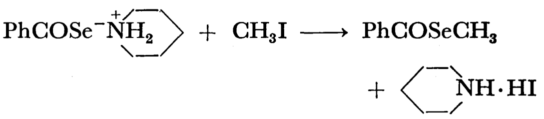
First, diacyl diselenides were prepared by a new, convenient method. The oxidation of a mixture of selenocarboxylic acid and sodium selenocarboxylate, which had been prepared by the reaction of acyl chlorides and sodium hydrogen selenide in ethanol, gave diacyl diselenides in good yields, as is shown in Table 1.[4] Next, diacyl selenides were obtained in good yields by the deselenization of diacyl diselenides. That is, the diacyl diselenides readily reacted with an equimolar amount of triphenylphosphine in benzene to give diacyl selenides and triphenylphosphine selenide. Diacyl selenides were isolated in good yields by the recrystallization of the resulting mixture from hexane–ether. The results and some properties are summarized in Table 2.

Distearoyl selenide was also prepared by the one-step reaction of stearoyl chloride with sodium selenide in benzene. The recrystallization of the crude product from benzene gave distearoyl selenide in a 67% yield, while small amounts of distearoyl diselenide and octadecylidene bis(selenostearate) were obtained as byproducts. On the other hand, attempts to use the same method for the preparation of dibenzoyl selenide were unsuccessful, though some of the dibenzoyl diselenide was isolated.

Reactions of Dibenzoyl Selenide with Amines. Jensen *et al.*[2] have described that dipropionyl selenide reacted with aniline to form 2 mol of propionanilide. However, when dibenzoyl selenide was treated with 2 mol of piperidine at 0 °C, piperidinium selenobenzoate (**3**) was isolated in a 79% yield. The piperidinium salt (**3**) was fairly stable in the solid state and did not change when left standing for a day under nitrogen. However, the salt (**3**) decomposed in ether at ordinary temperatures to give 1-benzoylpiperidine, with the concurrent evolution of hydrogen selenide (Scheme 2). The salt was confirmed by elemental analysis and by a study of its IR and NMR spectra. That is, in the IR spectrum the characteristic multiple absorption bands (νNH) at 2500—3000 cm^{-1} and a carbonyl absorption band at 1550 cm^{-1} were observed. The NMR spectrum showed peaks at 1.14 (6H, piperidine), 3.22 (4H, piperidine), 7.48, 8.28 (5H, C_6H_5), and near 9.4 ppm (about 2H, NH_2). Furthermore, the structure of the salt was chemically suported by the formation of methyl selenolbenzoate in a 90% yield by the reaction of the salt with methyl iodide in dry ether.



Scheme 2.



In a similar way, the reactions of bis(p-chlorobenzoyl) selenide and bis(p-methylbenzoyl) selenide with piperidine gave the corresponding piperidinium salts in 79 and 82% yields, respectively. Though, attempts to isolate the analogous adducts of dibenzoyl selenide with morpholine or dibutylamine failed, the infrared spectra of the oily substances, obtained by evaporating the solvent from the reaction mixture, showed multiple

Table 1. Synthesis and properties of diacyl diselenides (RCOSeSeCOR)

Compound	R	Yield %	Mp °C	Selenium Found(Calcd) %	IR, cm^{-1} (CCl$_4$) $\nu_{C=O}$	UV, nm (cyclohexane) λ_{max} (log ε)
2a	C_6H_5	77	131.0—132.0	42.55 (42.90)	1741 1700	242 (4.47) 281 (3.97)
2b	p-$CH_3C_6H_4$	80	110.0—111.5	39.41 (39.86)	1744 1704	253 (4.51) 280 (4.12)
2c	p-ClC_6H_4	81	122.0—124.0	35.75 (36.13)	1739 1700	253 (4.53) 285 (4.10)
2d	p-$CH_3OC_6H_4$	65	106.0—107.0	36.20 (36.88)	1746 1703	276 (4.53) 285$^{a)}$
2e	n-$C_{17}H_{35}$	86	79.8— 80.3	22.73 (22.79)	1732	244 (3.56)

a) Shoulder.

Table 2. Synthesis and properties of diacyl selenides (RCOSeCOR)

Compound	R	Yield %	Mp °C	Selenium Found(Calcd) %	IR, cm^{-1} (CCl$_4$) $\nu_{C=O}$	UV, nm (cyclohexane) λ_{max} (log ε)
1a	C_6H_5	88	61.5— 62.3	27.08 (27.30)	1737 1685	252 (4.34) 285 (3.86)
1b	p-$CH_3C_6H_4$	93	90.0— 91.0	24.72 (24.89)	1738 1690	263 (4.47) 303 (3.85)
1c	p-ClC_6H_4	91	118.5—120.0	21.88 (22.05)	1737 1686	263 (4.53) 304 (3.89)
1d	p-$CH_3OC_6H_4$	77	77.8— 80.2	22.33 (22.61)	1735 1687	282 (4.51) 305$^{a)}$
1e	n-$C_{17}H_{35}$	98	75.3— 75.8	12.74 (12.86)	1775 1715	261 (3.15)

a) Shoulder.

Table 3. Methanolysis of distearoyl selenide at 50 °C

Reaction conditions			Yield$^{a)}$ Mole ratio(%)		
Selenide	Gas	Time h	**1e**	**2e**	Ester$^{b)}$
1e	N_2	10	—	—	100
1e	N_2	0.5	22	12	66
1e	air	0.5	5	27	67
2e	N_2	0.5	10	71	19

a) The yields of these products were obtained by the UV method (Ref. 8). b) Methyl stearate.

bands(νNH) at 2500—3000 cm^{-1} and a carbonyl absorption band at 1550 cm^{-1}. These results may show that the reaction of diacyl selenide with amine gives, at first, the amine salt and amide, and that then the salt decomposes to give amide, with the evolution of hydrogen selenide.

Methanolysis of Distearoyl Selenide. It is known that the alcoholysis of diacyl sulfides gives the thio acid and the ester.[5] On the other hand, a methanolysis of distearoyl selenide (**1e**) in both a stream of nitrogen and air gave methyl stearate, distearoyl diselenide (**2e**), and **1e**, with the concurrent evolution of hydrogen selenide, but selenostearic acid was not obtained. On the other hand, as is shown in Table 3, in case of the reaction in a stream of air, the yield of **2e** was 27%, and in case of the reaction in a stream of nitrogen, that of **2e** was 12%, whereas the yields of **1e** were 5 and 22%, respectively. Furthermore, the reaction mixtures comsumed iodine in methanol. These results show that **2e** may be produced by the oxidation of selenostearic acid. That is, selenostearic acid may be formed by the methanolysis of **1e**, and the acid may change to **1e** with the evolution hydrogen selenide or may be oxidized to give **2e**, as is shown in the following equations:

$$\mathrm{RCOSeCOR + CH_3OH \longrightarrow [RCOSeH] + RCOOCH_3,} \quad (1)$$

$$\mathrm{2[RCOSeH] \longrightarrow RCOSeCOR + H_2Se,} \quad (2)$$

$$\mathrm{2[RCOSeH] \xrightarrow{(O)} RCOSeSeCOR + H_2O,} \quad (3)$$

$$\mathrm{RCOSeSeCOR + CH_3OH \longrightarrow [RCOSeH] + RCOOCH_3 + Se + H_2Se.} \quad (4)$$

These equations are supported by the reaction of **2e** with methanol in a stream of nitrogen to give **1e**, methylstearate and elemental selenium, with the concurrent evolution hydrogen selenide (Eq. 4).

Experimental

Synthesis of Dibenzoyl Diselenide. Hydrogen selenide, generated from Al_2Se_3 (0.80 mol)[7] and dilute hydrogen chloride and dried by being passed through a $CaCl_2$-tube, was led into a solution of sodium ethoxide (0.60 mol) in 400 ml of ethanol at 0 °C. Then, 71 g (0.50 mol) of benzoyl chloride was slowly added to the solution at 0 °C. After the stirring had continued for another 3 h, the mixture was treated with 100 g of iodine in ethanol and 5% aqueous

K_2CO_3. The organic layer was extracted with benzene, and the benzene solution was washed with aqueous $Na_2S_2O_3$ and then water, and dried over Na_2SO_4. The solvent was evaporated, and the residue was recrystallized from benzene-ether. Yield, 70.8 g (77%); mp 131—132 °C (lit,[1] 129—130 °C).

Synthesis of Dibenzoyl Selenide. A mixture of equimolar amounts of dibenzoyl diselenide (11.0 g; 0.03 mol) and triphenylphosphine (7.9 g; 0.03 mol) in benzene (150 ml) was stirred at room temperature for 1 h. After the benzene had then been evaporated under reduced pressure, ether was added to the residue. The resulting insoluble part (Ph_3PSe; mp 179—181 °C) was filtered off. After the ether had been removed from the filtrate, recrystallizations of the residue solid from hexane-ether gave 7.6 g (88%) of dibenzoyl selenide as white crystals; mp 60—61 °C (lit,[1] 61—62 °C).

Synthesis of Distearoyl Selenide by the Reaction of Stearoyl Chloride with Sodium Selenide. In a four-necked flask, 300 ml of ammonia dried by being passed through CaO-tube was liquefied, and then metal sodium (2.3 g; 0.10 mol) was added. Thereafter, elemental selenium (3.95 g; 0.05 mol) was slowly added to the solution at −40 °C under vigorous stirring. After the stirring had been continued for another 2 h, a small portion of selenium or sodium was added, as required. (If the solution become orange, a small quantity of sodium was added, or if it showed blue, a small quantity of selenium was added). Then, the solution turned white. After the solvent had been completely removed, to the residue in dry benzene (200 ml) stearoyl chloride (30.3 g; 0.10 mol) was added, drop by drop, at 50 °C and the stirring was continued for another 3 h. After the removal of the insoluble part from the reacting mixture by filtration, the solvent was removed. Recrystallizations of the residue from benzene gave 20.5 g (67%) of distearoyl selenide; mp 75.3—75.8 °C; Se 12.78% (Calcd for $C_{36}H_{70}O_2Se$: 12.86%), 1.5 g of distearoyl diselenide; mp 79.8—80.3 °C; Se 22.73% (Calcd for $C_{36}H_{70}O_2Se_2$: 22.79%), and 0.8 g of $(C_{17}H_{35}COSe)_2CHC_{17}H_{35}$; mp 58—59 °C; Se 16.67% (Calcd for $C_{54}H_{106}O_2Se_2$: 16.70%) νC=O 1709 cm^{-1}, νC-Se 945 cm^{-1}; NMR peaks 4.82 (–CH–, 1H, T,) 2.59 ($-CH_2CO-$, 4H, T), 1.25 ($-CH_2-$, about 92H, S) and 0.83 ppm ($-CH_3$, 9H, T).

Reaction of Dibenzoyl Selenide with Piperidine. A mixture of dibenzoyl selenide (2.90 g; 10 mmol) and piperidine (1.70 g; 20 mmol) in 50 ml of anhydrous ether was stirred at 0 °C for 30 min. The resulting precipitated were collected from the reaction mixture, and recrystallizations of the precipitate from dichloromethane-hexane gave 2.13 g (79%) of piperidinium selenobenzoate. The filtrate was concentrated under reduced pressure, giving 2.28 g (128%) of 1-benzoylpiperidine and a small amount of elemental selenium.

Reaction of Piperidinium Selenobenzoate with Methyl Iodide. The reaction of piperidinium selenobenzoate (1.0 g; 3.7 mmol) with methyl iodide (2.6 g) in 20 ml of dry ether at room temperature gave methyl selenolbenzoate (0.66 g, 90%; bp 105—106 °C/6 mmHg). The ester was identified by a comparison of its IR spectrum with that of an authentic sample.

Reaction of Distearoyl Selenide with Methanol. Methanol (15 ml) was added to a solution of 615 mg of distearoyl selenide in benzene (30 ml). The mixture was heated at 50 °C by means of N_2 gas. After 30 min, the reaction mixture was cooled and extracted with ether. The ether solution was washed with water, dried, and concentrated, giving a crystalline residue. Distearoyl selenide, distearoyl diselenide, and methyl stearate were obtained by the recrystallization of the residue, while the hydrogen selenide was evaporated during the reaction. We found nothing else. The yields (Table 3) of these products in the residue were calculated by fitting a equation[8] to extinction at 244 and 261 nm.

References

1) L. Szperl and W. Wiorogorski, *Rocz. Chem.*, **12**, 71 (1932)

2) K. A. Jensen, L. Bøje, and L. Henriksen, *Acta Chem. Scand.*, **26**, 1465 (1972).

3) H. Ishihara and Y. Hirabayashi, *Chem. Lett.*, **1976**, 203.

4) Diacyl diselenides were also obtained by the reaction of acyl chlorides with sodium diselenide in benzene; yields: **2a**, 64%; **2b**, 44%; **2e**, 58%.

5) Y. Hirabayashi, M. Mizuta, and T. Mazume, *Bull. Chem. Soc. Jpn.*, **38**, 1099 (1965).

6) All the melting points are uncollected. The IR, UV, and NMR spectra were determined on Jasco IR A-2, Shimadzu UV-200, and Hitachi-Perkin Elmer R-22 (90 MHz) spectrometers, respectively.

7) H. S. Booth, *Inorg. Synth.*, Vol. 2, 184 (1939).

8) D. T. Englis and D. A. Skoog, *Ind. Eng. Chem., Anal. Ed.*, **15**, 748 (1943).