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Organic Selenium Compounds

XVIII.* On the Existence of Monoselenocarboxylic Acids

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A compound described in the literature as selenobenzoic acid has been shown to be dibenzoyl diselenide. The true selenobenzoic acid is a very unstable liquid that reversibly splits off hydrogen selenide to form dibenzoyl selenide. In air it is very easily oxidized to dibenzoyl diselenide which is also formed in the absence of oxygen together with benzylidene bis(selenobenzoate).

Under conditions similar to those used for the preparation of monothiocarboxylic acids from acyl halides and hydrogen sulfide, propionyl chloride and hydrogen selenide gave dipropionyl selenide instead of selenopropionic acid.

SELENOBENZOIC ACID

A compound stated to be selenobenzoic acid, C_6H_5COSeH, has been described twice in the literature. Mingoia [1] obtained a solid with m.p. 133°C from the reaction of benzoyl chloride with MgBr(SeH), and Lewis [2] obtained an apparently identical compound from the reaction of benzoyl chloride and hydrogen selenide in pyridine. Although the high melting point (thiobenzoic acid melts at 24°C) and the reported stability of the compound in air cast severe doubt on this result, it has been reported without comments in the chemical handbooks (Beilstein, Houben-Weyl, Rodd). We have, however, found that this compound is, in fact, dibenzoyl diselenide, which was described by Szperl and Wiorogórsky [3] as one of the reaction products of benzoyl chloride and hydrogen selenide in the presence of aluminium chloride. Since neither Mingoia nor Lewis took special precautions to protect the reaction mixture against air, it is reasonable that they should have obtained the diselenide. This can, however, also be obtained from selenobenzoic acid in a redox reaction in the absence of air (see below). Mingoia stated as proof for the acidic character of his compound that it was soluble in ammonia, however, with copious forma-

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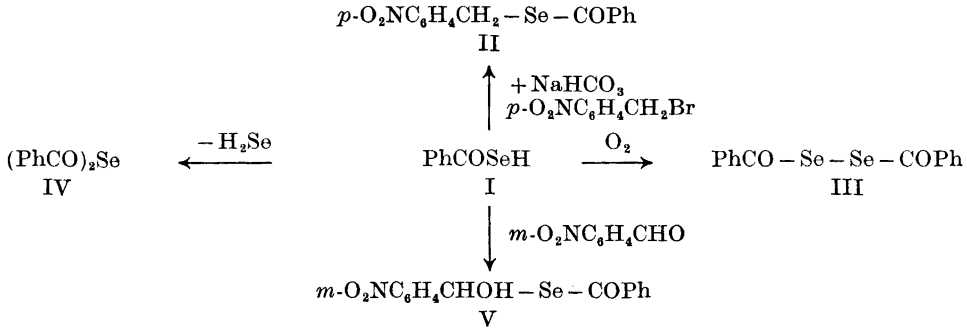
tion of red selenium. The latter observation is consistent with the behaviour of diselenides which are readily cleaved by nucleophiles with the formation of selenium (see also Experimental).

The primary product of the reaction of benzoyl chloride with hydrogen selenide in pyridine separates as an unstable pink oil on addition of excess sulfuric acid to the reaction mixture. It is readily soluble in most organic solvents and could be purified by extraction with ether, re-extraction from the filtered solution with sodium hydrogencarbonate, followed by precipitation with dilute sulfuric acid. Althouth it has not been possible to obtain an analytically pure sample the following properties (*cf.* Scheme 1) indicate that this substance is selenobenzoic acid (I):



Scheme 1.

(a) It is readily soluble in aqueous sodium hydrogencarbonate without formation of selenium and is reprecipitated from this solution with dilute sulfuric acid.

(b) Its ^{1}H NMR spectrum showed a multiplet ($\tau = 1.8 - 2.8$) of five protons and a singlet ($\tau = 6.15$) of one proton.

The position of the latter signal corresponds to a strongly acid Se – H compound without any appreciable content of an O – H tautomer. The absence of ^{77}Se satellites indicates rapid exchange and the position of the signal is somewhat dependent upon the presence of impurities, such as ether.

(c) Treatment of its solution in sodium hydrogencarbonate with *p*-nitrobenzyl bromide yielded Se-(*p*-nitrobenzyl) selenobenzoate (II).

(d) In the presence of air, dibenzoyl diselenide (III), m.p. 132°C, was formed.

(e) *In vacuo* or in a stream of an inert gas it lost hydrogen selenide with the formation of dibenzoyl selenide (IV), m.p. 62°C. This process is reversible but is accompanied by an irreversible redox process by which dibenzoyl diselenide and benzylidene bis(selenobenzoate) (VI) are formed.

$$5\ \mathrm{PhCOSeH} \rightarrow \mathrm{III} + \mathrm{PhCH(SeCOPh)_2} + \mathrm{H_2Se} + \mathrm{H_2O}$$

(f) With *m*-nitrobenzaldehyde *Se*-[hydroxy(*m*-nitrophenyl)-methyl] selenobenzoate (V) was formed.

In our first attempts to duplicate the preparation of selenobenzoic acid according to Lewis [2] we obtained dibenzoyl diselenide along with a considerable amount of a compound with m.p. 149°C, which according to analyses and its ^{1}H NMR spectrum was *Se,Se'*-benzylidene bis(selenobenzoate) (VI). Later we had difficulties in reproducing this result until it was found that the reaction was catalyzed by pyridine which had not been completely removed in the first experiments. Benzaldehyde might conceivably have been an intermediate in the formation of the benzylidene compound. However, under the conditions of the experiment selenobenzoic acid did not give VI with benzaldehyde, and, although it reacted with *m*-nitrobenzaldehyde, the reaction product was not a benzylidene bis(selenobenzoate) but compound V.

DIPROPIONYL SELENIDE

Aliphatic monothiocarboxylic acids can be prepared in relatively good yields from the reaction of acyl halides with hydrogen sulfide in anhydrous pyridine [4] and the acids can be distilled *in vacuo* without decomposition. Attempts to use a similar method for the preparation of monoselenocarboxylic acids were insuccessful. Less than 10 % of distillable products were obtained from acetyl, propionyl, or isobutyryl chloride, while most of the reaction products remained in the distillation flask as dark tars. According to titration analyses and infrared spectra the distillates were not the expected acids but rather the diacyl selenides, although in impure states. The propionyl derivative, VII, was prepared in the pure state and in much better yields by using propionyl chloride and an equimolar amount of pyridine dissolved in diethyl ether.

Dipropionyl selenide (VII) is a colourless liquid which could be distilled without decomposition under reduced pressure. It was characterized by its ^{1}H NMR spectrum and infrared spectrum. Like the acid anhydrides it shows a doubling of the carbonyl frequency with a spacing of *ca.* 60 cm^{-1}. This also applies to dibenzoyl selenide and the above-mentioned diacetyl and diisobutyryl selenide.

The isolation of diacyl selenides instead of aliphatic selenocarboxylic acids indicates that the latter will be unstable. However, whether they may be formed from the diacyl selenides and hydrogen selenide at higher pressure or lower temperature has still to be investigated.

Dipropionyl selenide rapidly dissolved in water on addition of sodium hydroxide, consuming two equivalents of base. Usually a small amount of a voluminous precipitate is formed during neutralization, probably a diacyl polyselenide. With sodium methanolate VII formed the selenopropionate ion which could be trapped by reaction with benzyl bromide to give *Se*-benzyl selenopropionate (VIII). With aniline 2 mol of propionanilide was formed. This indicates that a selenocarboxylic acid may function as an acylating agent.

$$\underset{\text{VII}}{(EtCO)_2Se} \xrightarrow{+MeO^-} EtCOSe^- \xrightarrow{+PhCH_2Br} \underset{\text{VIII}}{EtCO-Se-CH_2Ph}$$

$$\underset{\text{VII}}{(EtCO)_2Se} + 2\ PhNH_2 \longrightarrow 2\ PhNH-COEt + H_2Se$$

EXPERIMENTAL

The infrared spectra were recorded on a Perkin-Elmer Model 337 grating spectrophotometer and the NMR spectra on a Varian A60 A spectrometer.

The preparations were generally performed under such conditions that oxygen was rigorously excluded.

Selenobenzoic acid (*I*). To dry pyridine (100 ml) was added benzoyl chloride (100 mmol), the temperature being kept at *ca.* −15°C. Hydrogen selenide, generated from Al_2Se_3 (11 g) with 2 M H_2SO_4 and dried through a $CaCl_2$-tube was passed through the reaction mixture in a nitrogen stream. The reaction took 2 h at −20°C. Ether (250 ml), filtered through alumina and flushed with nitrogen, was added to the reaction mixture followed by oxygen-free 2 M H_2SO_4 (400 ml). The isoluble material was filtered off and the phases were separated. The aqueous phase was extracted with an additional 50 ml of ether and the ether extracts were re-extracted with 1 M $NaHCO_3$ (100 ml). Dissolved ether was removed from the basic solution by a stream of nitrogen and the subsequent addition of 2 M H_2SO_4 precipitated a pink oil which was separated and dried with anhydrous $CaSO_4$. Yield 10.3 g. The oil did not crystallize on cooling and could not be distilled. On heating it decomposed with evolution of H_2Se and formation of *ca.* 10 (judged from TLC) undefined products. The ^1H NMR spectrum of the substance (neat, 40°C) showed in addition to weak signals from ether (estimated content *ca.* 1 %) only signals corresponding to selenobenzoic acid: $\tau = 2.15 - 2.90$ (m, 5H); $\tau = 6.15$ (s, 1H).

The oil is easily soluble in both polar and non polar solvents; it dissolves in aqueous NaOH with a yellow colour. In air the oil rapidly solidifies with the formation of dibenzoyl diselenide (III). In the absence of air it slowly solidifies with evolution of H_2Se and the formation of dibenzoyl selenide (IV), dibenzoyl diselenide (III), and benzylidene bis(selenobenzoate) (VI). In a flask equipped with an outlet for H_2Se, the disappearance of I took more than 3 days; addition of a few drops of pyridine caused the reaction to proceed within 12 h. In a sealed flask the reaction was incomplete, *i.e.* some I remained even after a month, and a considerable pressure of H_2Se was generated.

The insoluble byproduct from the preparation of I (4.8 g) was identified as dibenzoyl diselenide (III), m.p. 130 − 131°C (hexane). Evaporation of the ether phase yielded an additional 3.35 g of a solid consisting of a mixture of III, IV, and VI.

Se-(p-*Nitrobenzyl*) *selenobenzoate* (*II*). The crude selenobenzoic acid (2.5 mmol) was dissolved in 1 M $NaHCO_3$ (2.5 ml) and added to a solution of *p*-nitrobenzyl bromide (2.5 mmol) in dimethylformamide (25 ml). The initial yellow colour of the selenobenzoate disappeared immediately. On addition of water and cooling a colourless solid separated. Yield 96 % (0.74 g, recryst. methanol). M.p. 107 − 109°C. (Found: C 52.70; H 3.57; N 4.35. Calc. for $C_{14}H_{11}NO_3Se$: C 52.50; H 3.43; N 4.37.) ^1H NMR spectrum ($CDCl_3$; 40°C): $\tau = 1.9 - 2.9$ (m, 9H); $\tau = 5.70$ (s, 2H, satellites $J(^{77}Se\ H) = 13$ Hz).

Dibenzoyl diselenide (*III*). Selenobenzoic acid (0.5 ml) was dissolved in ether (25 ml) and stirred in an open flask for 3 h. The solution became colourless and a yellowish solid separated. Yield 0.50 g. M.p. 130 − 131°C (lit. 129 − 130,[3] 133[1]). This compound is also formed when oxygen is bubbled through a solution of dibenzoyl selenide (IV) in ethanol (30°C, 1 h). After 3 recrystallizations from ethanol the m.p. was 131°C. (Found: C 45.5; H 2.71; Se 43.2. Calc. for $C_{14}H_{10}O_2Se_2$: C 45.9; H 2.79; Se 42.9.) Boiling of the ethanol solution during recrystallization has to be avoided, otherwise some selenium is formed; *cf.* that Mingoia [1] described his compound with m.p. 133°C as pink.

Reaction of III with ammonia. 1 M ammonia in methanol (2.5 ml) was added to a boiling solution of III (1 mmol) in methanol (50 ml) and *p*-nitrobenzyl bromide (1 mmol) rapidly added to the resulting mixture. Precipitated selenium (72 mg, 91 %) was filtered off and the filtrate evaporated to dryness. On recrystallization of the residue twice from toluene, 80 mg (66 %) of benzamide was isolated. Evaporation of the mother liquor and recrystallization of the residue from methanol yielded 220 mg (69 %) of II.

Dibenzoyl selenide (*IV*). Selenobenzoic acid (I, 1.3 g) was dissolved in toluene and the solution evaporated *in vacuo* at 60°C to give a colourless oil which solidified on cooling. The solid was dissolved in boiling hexane (20 ml). On cooling the solution to room temperature a mixture of III and IV separated. The filtered solution was run through Al_2O_3 and cooled to −20°C to give a small amount of IV, m.p. 60 − 61°C (lit.[3] 61 − 62). This compound has also been obtained in relatively good yield (27 %; recryst. ethanol) by

following the procedure of Mingoia [1] but in the absence of air. (Found: C 57.57; H 3.46; Se 27.41. Calc. for $C_{14}H_{10}O_3Se$: C 57.90; H 3.45; Se 27.60.)

Dibenzoyl selenide cannot be extracted from an ether solution by dilute sodium hydroxide. However, when the ether solution is saturated with hydrogen selenide the almost colourless solution becomes pink and the solute can now be completely extracted with dilute NaOH. On addition of hydrochloric acid to the basic solution selenobenzoic acid is precipitated as a pink oil.

Se-(*Hydroxy*-(m-*nitrophenyl*)*methyl*) *selenobenzoate* (*V*). *m*-Nitrobenzaldehyde (5 mmol) was dissolved in toluene (20 ml) and selenobenzoic acid (5 mmol) was added. The red colour of I disappeared immediately and subsequent cooling caused precipitation of V. Yield 82 %. M.p. 76 – 80°C; the product could not be recrystallized without decomposition. (Found: C 49.95; H 3.37; N 4.05. Calc. for $C_{14}H_{11}NO_4Se$: C 50.00; H 3.27; N 4.17.) Addition of an excess of selenobenzoic acid did not result in the formation of a bis(selenobenzoate).

Se,Se′-*Benzylidene bis*(*selenobenzoate*) (*VI*). When a trace of pyridine is added to selenobenzoic acid (I) it solidifies in the course of *ca.* 1 day when kept in an inert atmosphere (argon). The resulting product is a mixture of III and VI with varying amounts of IV. Repeated recrystallizations from propanol yielded colourless crystals of VI with m.p. 149 – 150°C, in accord with Ref. 3. (Found: C 55.12; H 3.93; Se 34.40. Calc. for $C_{21}H_{16}Se_2O_2$: C 55.02; H 3.52; Se 34.45.) ^{1}H NMR spectrum ($CDCl_3$, 40°C): $\tau = 1.9 - 2.7$ (m, 15 H); $\tau = 3.48$ (s, 1 H). The compound is easily soluble in benzene but only slightly soluble in alcohols. It is very stable towards acids but is hydrolyzed by NaOH with the formation of benzaldehyde.

Better yields are obtained by recrystallizing the crude product from heptane and boiling the residue from the mother liquor with 1-butanol which decomposes the diselenide with the formation of selenium: 1.3 g of I yielded 65 mg of VI (m.p. 149 – 151°) on cooling to 30°C and 50 mg of III (m.p. 125 – 129) on cooling to 20°C. The residue from the mother liquor yielded 20 mg of VI (m.p. 147 – 149) on boiling with 1-butanol, filtration of the solution, cooling, and recrystallization of the separated crystals from heptane.

Dipropionyl selenide (*VII*). Propionyl chloride (9 g) dissolved in dry ether (300 ml) was slowly added, at – 10°C, to a stirred solution of pyridine (8 g) in dry ether (300 ml). Hydrogen selenide, generated from 6 g of Al_2Se_3 with dilute sulfuric acid and dried through a $CaCl_2$-tube was introduced into the reaction mixture in a nitrogen stream over a period of 3 h. The reaction mixture was washed with water, dried (Na_2SO_4), and the ether was removed by evaporation. The residue was distilled twice under reduced pressure. Yield 5.5 g (29 %) of VII with b.p. 103 – 105°C/23 mmHg. (Found: C 37.15; H 5.13. Calc. for $C_6H_{10}O_2Se$: C 37.28; H 5.17.) ^{1}H NMR spectrum (neat, 40°C): $\tau = 7.14$, (q, $J = 7$ Hz, 2H); $\tau = 8.85$ (t, $J = 7$ Hz, 3 H). IR spectrum: 1720 vs, 1780 m (C=O); 900 vs (Se – CO).

On addition of aniline to a solution of 10 mmol of VII in ether 16 mmol of propionanilide (recryst. toluene-hexane, m.p. 103°C) could be isolated, corresponding to a reaction of 1 mol of VII with 2 mol of aniline.

Se-*Benzyl selenopropionate* (*VIII*). (a) Phenylmethaneselenol (8.5 g) dissolved in ether (20 ml) was added to a solution of propionyl chloride (4.6 g) and pyridine (6 ml) in ether (15 ml), prepared as above. The reaction mixture, protected by a nitrogen atmosphere, was left for 1 h, filtered and washed with 0.4 M sulfuric acid. The dried (Na_2SO_4) ether phase was concentrated and distilled to give 7.0 g VIII (63 %), b.p. 161 – 163°C/25 mmHg. (Found: C 52.62; H 5.30. Calc. for $C_{10}H_{12}OSe$: C 52.82; H 5.32.) ^{1}H NMR spectrum (CS_2, 40°C): $\tau = 2.88$ (s, 5 H); $\tau = 5.98$ (s, 2 H; satellities: $J(^{77}Se\ H) = 11$ Hz); $\tau = 7.43$ (q, 2 H); $\tau = 8.87$ (t, 3 H).

(b) To a solution of VII (0.97 g) in ether (20 ml) was added 2 M sodium methanolate (2.5 ml) followed by benzyl bromide (0.86 g). The reaction mixture was left for 1 h and then filtered. On removal of the ether and distillation of the residue *in vacuo* 1.0 g (83 %) of VIII was obtained.

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