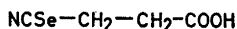
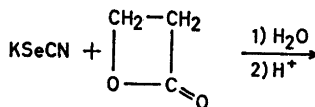


5. Patterson, W. J. and du Vigneaud, V. J. *J. Biol. Chem.* **111** (1935) 393.
6. Bengtsson, A. *To be published.*
7. Gould, E. S. *Anal. Chem.* **23** (1951) 1502.
8. Painter, E. P. *J. Am. Chem. Soc.* **69** (1947) 229.
9. Gardner, J. H. and Naylor, Jr., C. A. *Org. Syn. Coll. Vol. II*, 1943, p. 526.

Received March 16, 1967.

the preparation of β -thiocyanatopropionic acid, an improved method of synthesis of the corresponding β -selenocyanatopropionic acid (I) has now been developed.



I

Scheme 1

The Reaction between β -Propiolactone and Selenium-containing Reagents

LARS-BÖRGE AGENÄS and
BJÖRN PERSSON

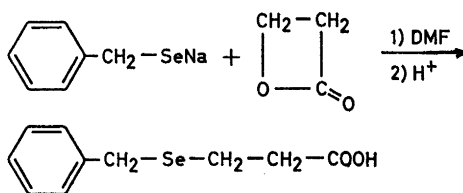
*Chemical Institute, University of Uppsala,
Uppsala, Sweden*

The reaction between some γ - and δ -lactones and sodium benzyl selenolate has earlier been studied by one of us,^{1,2} among other things for the purpose of preparing the corresponding seleno-substituted carboxylic acids through a simple and convenient method of synthesis. The corresponding γ - and δ -benzylseleno-substituted carboxylic acids were obtained in this way in satisfactory yield. As a consequence of these experiments, it was quite obvious to extend this investigation also to β -lactones. From the investigation of the reactivity of β -propiolactone by Gresham *et al.*³ it is known that this compound easily reacts with potassium thiocyanate along with many other reagents. The reaction was performed in a water solution and in this way an almost quantitative yield of β -thiocyanatopropionic acid was obtained. The corresponding β -selenocyanatopropionic acid was earlier prepared by Fredga,⁴ who reacted potassium selenocyanate with an aqueous solution of neutralized β -chloropropionic acid. The method gives a good yield but always an amount of elemental selenium is obtained as a by-product, arising from the acidic decomposition of unreacted potassium selenocyanate. Following the method by Gresham *et al.* for

Thus, an aqueous solution of potassium selenocyanate was prepared and β -propiolactone was added at room temperature. After acidifying the reaction mixture, a quantitative yield of I was obtained after extraction.

For a comparison with the earlier experiments performed with γ - and δ -lactones, an attempt to react β -propiolactone with potassium selenocyanate in a dimethyl formamide solution was also made. However, the potassium selenocyanate is only slightly soluble in this solvent and no reaction was observed after a reasonable time.

Another reagent frequently used for the introduction of a selenium substituent into an organic molecule, is benzyl selenol. In this investigation, sodium benzyl selenolate was prepared by adding the selenol to a solution of sodium methanolate. After evaporating the resulting solution almost to dryness, a dimethyl formamide solution of β -propiolactone was added at room temperature. After acidifying the resulting mixture, an almost quantitative yield of β -benzylselenopropionic acid (II) was obtained.



II

Scheme 2

This substance (II) has earlier been described by Fredga,⁵ who prepared it through the reaction of benzyl chloride with an aqueous solution of neutralized β -hydroselenopropionic acid. The method of preparation described in this paper is very rapid and gives an almost quantitative yield.

By the experiments described above it is shown, that β -propiolactone reacts, as expected, very fast also with selenium-containing nucleophilic reagents and in this way a simple method for the preparation of β -selenosubstituted propionic acids has been obtained. The reaction is equally well performed in water as well as in dimethyl formamide solutions, provided the reagent in question is soluble in the solvent.

Experimental. The infrared spectra were recorded using a Perkin-Elmer model 237 Infracord spectrophotometer. The selenium analyses were performed according to a micro-method developed by Bengtsson.⁶ This method is very similar to that of Gould.⁷ The melting-points are uncorrected.

β -Selenocyanatopropionic acid (I). A solution of 21.6 g (0.15 mole) of potassium selenocyanate⁸ in 75 ml of water was prepared and placed in a three-necked flask fitted with a dropping funnel, a mechanical stirrer, and a reflux condenser. To this solution 10.8 g (0.15 mole) of commercial β -propiolactone were added. The rate of the addition was maintained so that the reaction temperature did not exceed 25°. When all the lactone was added, the reaction mixture was acidified with concentrated hydrochloric acid and diluted with 50 ml of water. The mixture was thoroughly extracted with ether and the ether extracts were dried over magnesium sulfate. After evaporating the ether under vacuum, a

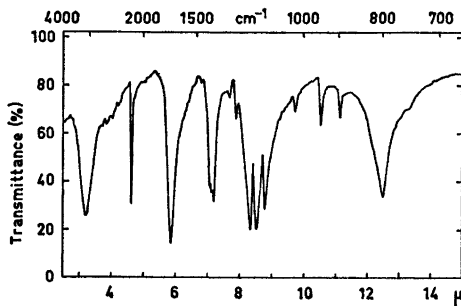


Fig. 1. Infrared spectrum of β -selenocyanatopropionic acid (I) in KBr-phase.

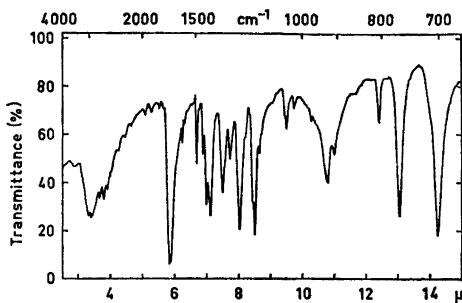


Fig. 2. Infrared spectrum of β -benzylselenopropionic acid (II) in KBr-phase.

yellowish oil was obtained, which solidified upon cooling. The yield of crude material was 26.7 g (100%), m.p. 48–54°. Three recrystallizations from benzene (norite) gave the analytical pure substance, m.p. 55–56°. (Found: C 26.98; H 2.91; Se 44.20; equiv. wt. 177.7. Calc. for $C_4H_6NO_2Se$: C 26.97; H 2.83; Se 44.34; equiv. wt. 178.05).

β -Benzylselenopropionic acid (II). In a three-necked flask, fitted with a dropping funnel, a mechanical stirrer, and a reflux condenser, a sodium methanolate solution was prepared from 1.25 g (0.055 atom) of sodium and 20 ml of absolute methanol. To this solution 9 g (0.055 mole) of benzyl selenol⁹ were added with stirring. The reddish-brown solution was evaporated almost to dryness with stirring under reduced pressure and to the remaining yellowish brown solid, a solution of 3.6 g (0.05 mole) of β -propiolactone in 50 ml of dimethyl formamide was added. An exothermic reaction immediately started and the lactone solution was added at such a rate, that the temperature did not exceed 35°. If necessary, cooling with an ice-bath was used. The reaction mixture was allowed to stand at room temperature with stirring for 2 h and finally 500 ml of water was added. The alkaline solution was extracted with ether to remove impurities, and acidified with dilute sulfuric acid. An emulsion was obtained, which was thoroughly extracted with ether. The combined ether extracts were washed with water to remove dimethyl formamide. After drying the ether solution over sodium sulfate, the ether was removed by distillation and the remaining oil solidified upon cooling. The yield of crude material was 12.0 g (98%), m.p. 69–73°. Repeated recrystallizations from light petroleum (norite) gave the analytically pure acid as colorless leaves, m.p. 73.5–75°. (Found: C 49.46; H 4.95; Se 32.37; equiv. wt. 242.3.

Calc. for $C_{10}H_{12}O_2Se$: C 49.38; H 4.98; Se 32.46; equiv. wt. 243.17).

Acknowledgements. We wish to express our sincere gratitude to Professor Arne Fredga and to Professor Folke Nydahl for all facilities placed at our disposal. A grant from the *Faculty of Mathematics and Natural Sciences, University of Uppsala* to one of us (L.-B. A.) is gratefully acknowledged. The carbon and hydrogen micro analyses were performed at the Central Analytical Laboratory, University of Uppsala and the microanalyses for selenium by Mrs. Lena Möller. In connection with this, we wish to express our gratitude to Dr. Arthur Bengtsson for all help with instruction on the microanalytical selenium method.

1. Agenäs, L.-B. *Arkiv Kemi* **24** (1965) 415.
2. Agenäs, L.-B. *Arkiv Kemi* **24** (1965) 573.
3. Gresham, T. L., Jansen, J. E., Shaver, F. W., Frederick, M. R., Fiedorek, F. T., Bankert, R. A., Gregory, J. T. and Beears, W. L. *J. Am. Chem. Soc.* **74** (1952) 1323.
4. Fredga, A. *J. prakt. Chem.* (2) **121** (1929) 56.
5. Fredga, A. *Svensk Kem. Tidskr.* **48** (1936) 91.
6. Bengtsson, A. *To be published.*
7. Gould, E. S. *Anal. Chem.* **23** (1951) 1502.
8. Waitkins, G. R. and Shutt, R. *Inorg. Syn.* **2** (1954) 186.
9. Painter, E. P. *J. Am. Chem. Soc.* **69** (1947) 229.

Received March 16, 1967.

Some Properties of a Ternary Sulfide Mo-Sn-S

ARNE W. ESPELUND

Metallurgisk Institutt, Norges tekniske høgskole, Trondheim, Norway

Metallic tin has been suggested as a reducing agent for molybdenite, MoS_2 .¹ The sulfur can be volatilized mainly as SnS , giving a metallic residue of molybdenum. In an attempt in our laboratory to measure the vapour pressures of the various univariant equilibria involved with subsequent examination of the products, the X-ray pattern of a new phase was obtained.

This compound could not be isolated by any conventional method from the other phases in the sample, and synthesis in quartz ampoules was resolved upon: Finely powdered molybdenum, sulfur, and tin were mixed together in certain proportions and sealed off under vacuum. When a certain temperature gradient was maintained along the ampoule — about 900 to 400°C — the highly exothermic reaction could take place without establishing an internal pressure causing destruction of the ampoule. The mixture was ground and given a second homogenizing treatment.

Upon microscopic examination black crystals with rectangular crystal faces were found.

Debye-Scherrer photographs showed the pattern of a single phase for a mixture with an atomic ratio Mo:Sn:S close to 6:1:7. It conjugated with the other substances MoS_2 — Mo_3S_3 —Mo—Sn, so that straight lines emerge from the ternary compound to each of these phases in a conventional ternary diagram. There was no variation in the θ -values from one three-phase combination to another, indicating a limited homogeneity range.

The pattern obtained, supplemented with electron diffraction suggests a unit cell of orthogonal symmetry. The observed lines are fairly well explained by assuming a pseudocubic unit cell with $a = 6.53$ Å, as shown in Table 1. Cubic unit cells with $a = 6.53\sqrt{2}$, 6.53×2 and $6.53\sqrt{3}$ were tried without complete resolution of all lines. Application of a Bunn chart for tetragonal crystals gives satisfactory indexing of the first lines with $a = b = 6.53$, $c = 9.23$ Å, i.e. $c \approx a\sqrt{2}$, but some lines at high θ -values could not be resolved.

Several attempts to produce single crystals of a suitable size failed.

Measurement of the specific gravity by means of pycnometer gave as result 5.69 ± 0.03 g/cm³. The stoichiometric proportion referred to above (6 Mo:1 Sn:7 S) renders as formula weight 919. The calculated formula weight of the content of a pseudocubic unit cell with $a = 6.53$ Å is 950, — in reasonable agreement with the former value.

This new compound with a metal to sulfur ratio apparently 1:1 appears to be interesting because the presence of tin stabilizes a monosulfide, which has not been obtained in the binary system Mo—S. A further investigation of its