

The molecular field theory (*cf.* Smart¹⁹) gives an exchange parameter J/k of 18.3 or 19.3°K on the basis of T_c -values reported to be 110^{5,6} or 116°K.⁷ However, the simple molecular field theory requires a θ/T_c ratio of 1, which differs from the observed values 1.46^{5,6} and 1.32.⁷ Improvement on the simple molecular field treatment is obtained by the various effective field approximations, of which *e.g.* the constant coupling approximation would predict $\theta/T_c = 1.22$ in the case of CoS₂. (It must be emphasized that the use of the constant coupling approximation leads to a considerable increase in the J/k -value. $J/k = 22.3$ or 23.5°K is obtained for $T_c = 110$ or 116°K.)

1. Lundqvist, D. and Westgren, A. *Z. anorg. allgem. Chem.* **239** (1938) 85.
2. Elliott, N. *J. Chem. Phys.* **33** (1960) 903.
3. Haraldsen, H. and Klemm, W. *Z. anorg. allgem. Chem.* **223** (1935) 409.
4. Haraldsen, H. *Z. anorg. allgem. Chem.* **224** (1935) 85.
5. Néel, L. and Benoit, R. *Compt. Rend.* **237** (1953) 444.
6. Benoit, R. *J. Chim. Phys.* **52** (1955) 119.
7. Heidelberg, R. F., Luxem, A. H., Talhouk, S. and Banewicz, J. *J. Inorg. Chem.* **5** (1966) 194.
8. Straumanis, M. E., Amstutz, G. C. and Chan, S. *Am. Mineralogist* **49** (1964) 206.
9. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
10. Roth, W. L. *J. Phys. Chem. Solids* **25** (1964) 1.
11. van Laar, B. *Phys. Rev.* **138** (1965) A584.
12. Scatturin, V., Corliss, L., Elliott, N. and Hastings, J. *Acta Cryst.* **14** (1961) 19.
13. Shirane, G. *Acta Cryst.* **12** (1959) 282.
14. Hulliger, F. *Helv. Phys. Acta* **32** (1959) 615.
15. Kjekshus, A. *Acta Chem. Scand.* **18** (1964) 2379.
16. Hastings, J. M., Elliott, N. and Corliss, L. M. *Phys. Rev.* **115** (1959) 13.
17. Goodenough, J. B. *Magnetism and the Chemical Bond*, Interscience, New York 1963.
18. Wollan, E. O. *Phys. Rev.* **117** (1960) 387.
19. Smart, J. S. *Effective Field Theories of Magnetism*, Saunders, Philadelphia — London 1966.

Received February 16, 1967.

The Synthesis of 2-Carboxy-dibenzyl Selenide

LARS-BÖRGE AGENÄS and
BJÖRN PERSSON

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

Unsubstituted and some alkyl-substituted five- and six-membered lactones have been studied by one of us^{1,2} for the purpose of using these compounds as starting materials in the syntheses of the corresponding γ - and δ -selenosubstituted carboxylic acids. This was made possible through their reaction with sodium benzyl selenolate in a dimethyl formamide solution. In this way a simple and convenient method of syntheses was developed. Recently the investigation was extended and β -propiolactone was studied for the same purpose as above, and we found, as expected, that this very reactive compound gives an almost quantitative yield of β -selenosubstituted propionic acids with different types of reagents.³

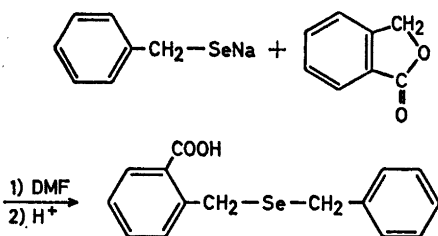
It was also of interest for us to investigate if other substituents than alkyl groups in the five-membered lactone ring permit the reaction with sodium benzyl selenolate in a dimethyl formamide solution. A preliminary report on our results will be given in this paper.

In the present investigation, it was considered of importance to ascertain whether an amino group as substituent in the lactone ring permits the reaction with sodium benzyl selenolate. So far, we have had no chance to make any experiment with α -amino- γ -butyrolactone, because it has not been possible for us to isolate it. This was certainly caused by a reaction very similar to that one observed by Sudo,⁴ who reports the rapid dimerization of α -amino- γ -butyrolactone into 3,6-(β -hydroxyethyl)-2,5-diketopiperazine. Our interest was thus directed towards the stable hydrobromide of the lactone in question, but in this case a too low solubility in dimethyl formamide prevented any reaction.

We have also made experiments with α -acetyl- and α -formyl- γ -butyrolactones, but also in these cases no reaction took place with sodium benzyl selenolate, because of decomposition of the lactones at the temperature necessary for the reaction.

Our interest was also directed towards aromatic substituents in the lactone ring. Thus α,α -diphenyl- γ -butyrolactone was treated with sodium benzyl selenolate, but no reaction occurred. The reason to the failure can be steric effects, but also other effects can be present.

Finally, phthalide was treated with sodium benzyl selenolate in dimethyl formamide solution and in this case the expected reaction takes place. A good yield of 2-carboxy-dibenzyl selenide was obtained when the reaction mixture was worked up in the usual way.



An attempt to debenzylate the product with sodium in liquid ammonia according to du Vigneaud,⁵ however, failed. A very complex product was obtained, which seems to contain some *o*-toluic acid. This suggests, that in this case both carbon-selenium bonds are broken by this treatment.

Our investigation of different substituted γ -lactones will be continued and especially those cases where no reaction has been obtained will be considered. It is our hope to be able to give a more detailed report on our results as soon as possible.

Experimental. The infrared spectrum was recorded using a Perkin-Elmer model 237 Infracord spectrophotometer. The selenium analysis was performed by a microanalytical method developed by Bengtsson,⁶ which is very similar to that one published by Gould.⁷ The melting points are uncorrected.

2-Carboxy-dibenzyl selenide. In a three-necked flask equipped 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 in 20 ml of absolute methanol. To this solution 9 g (0.055 mole) of benzyl selenol⁸ were added and the resulting reddish-brown solution was evaporated almost to dryness with stirring at a reduced pressure. To the remaining yellowish-brown solid, a solution of 6.7 g (0.05 mole) of

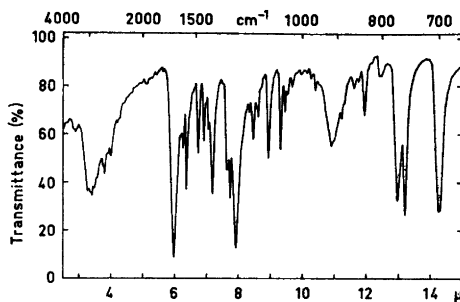


Fig. 1. Infrared spectrum of 2-carboxy-dibenzyl selenide in KBr-phase.

phthalide⁹ in 40 ml of dimethyl formamide was added and the mixture was heated to 120–130° for 5 h.

The dimethyl formamide was removed with stirring under vacuum and 400 ml of water were added to the brownish residue. The solution was extracted with ether to remove impurities and acidified with dilute sulfuric acid. An emulsion was obtained, which was extracted thoroughly with ether. The combined ether extracts were dried over magnesium sulfate. The ether was removed by distillation and the remaining yellow oil immediately solidified. The yield of crude material was 12.8 g (84%), m.p. 138–144°. Repeated recrystallizations from benzene (norite) gave the analytically pure product, m.p. 144–144.5°. (Found: C 59.12; H 4.59; Se 25.81; equiv. wt. 305.0. Calc. for C₁₆H₁₄O₂Se: C 59.02; H 4.62; Se 25.87; equiv. wt 305.22).

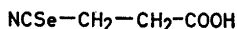
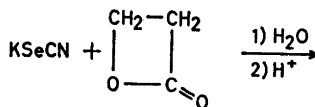
Acknowledgements. We wish to express our sincere gratitude to Professor Arne Fredga and Professor Folke Nydahl for all the facilities placed at our disposal. A grant from the Faculty of Mathematics and Natural Sciences, University of Uppsala, to one of us (L.-B. A) is gratefully acknowledged. The carbon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

1. Agenäs, L.-B. *Arkiv Kemi* **24** (1965) 415.
2. Agenäs, L.-B. *Arkiv Kemi* **24** (1965) 573.
3. Agenäs, L.-B. and Persson, B. *Acta Chem. Scand.* **21** (1967) 837.
4. Sudo, R. *Nippon Kagaku Zasshi* **79** (1958) 81; *Chem. Abstr.* **54** (1960) 5448.

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

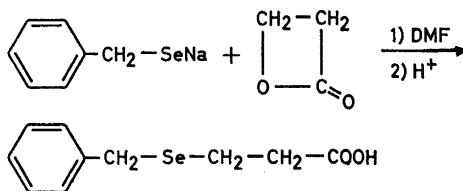
*Chemical Institute, University of Uppsala,
Uppsala, Sweden*

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