[Contribution from the Department of Chemistry, University of California at Los Angeles]

The Synthesis of Unsymmetrical Selenides

By Tod W. Campbell and James D. McCullough

During the course of an investigation of the effects of ring substituents on the dissociation constants of diphenylselenium dihalides[1,2] being carried out in this Laboratory, it was necessary to synthesize a large number of substituted diphenyl selenides. The symmetrically disubstituted compounds offer no special problem and are readily prepared in most cases by standard methods. Although a number of procedures appear in the literature for the synthesis of unsymmetrical selenides, RSeR′, it is felt that the new syntheses presented in this communication represent definite improvements.

Of the earlier methods, probably the best is that of Keimatsu[3] and co-workers who extend the well-known reaction of a diazonium salt[4] with an alkali selenide to produce symmetrical selenides. These workers substitute the sodium salt of a selenophenol for the alkali selenide used when a symmetrical product is desired. The yields are reported to be good. Other known methods include the reaction of a sodium selenophenolate with a compound containing active halogen, reaction of an arylselenium bromide on a Grignard reagent[5] and of powdered selenium on an unsymmetrical sulfone.[6] The yields in these latter procedures are not consistently good.

Two new synthetic methods are presented herein, the first being based on the reaction of a diaryldiselenide with a Grignard reagent

$$R_2Se_2 + R'MgBr = RSeR' + RSeMgBr \quad (1)$$

while the second is based on the reaction of an arylselenium monobromide with a mercury diaryl

$$R'SeBr + R_2Hg = RSeR' + RHgBr \quad (2)$$

Reactions similar to (1) have been noted. Wuyts[7] reported the reaction between diphenyl disulfide and ethylmagnesium bromide to give phenyl ethyl sulfide while Schönberg[8] reported interaction of phenyl lithium with diphenyl disulfide and diphenyl diselenide to give diphenyl sulfide and diphenyl selenide, respectively. Reaction (2) is an extension of that employed by Leicester[9] to produce symmetrical diaryl selenides by interaction of selenium tetrabromide and a mercury diaryl.

Both of the new reactions are rapid and result in good yields. Where less than 2–3 g. of product is required, the mercury diaryl synthesis is recommended because of its simplicity and the fact that the selenide is easily obtained in high purity and in practically quantitative yield. If larger quantities of the selenides are required, the Grignard synthesis is recommended because of its greater economy.

Experimental

Preparation of Diselenides.—The diselenides were prepared by one of the following procedures:

(1) Commercial selenium is made into a paste with methanol (to render it more easily wet by the aqueous solution) and treated with a 10% excess of 3 *M* aqueous potassium cyanide. The mixture warms and most of the selenium dissolves. After heating one-half hour on the sand-bath, the mixture is filtered. The concentration of the resulting solution of selenocyanate is found with sufficient accuracy by evaporation of a portion to dryness. From this solution the aryl selenocyanates were prepared by the method of Behagel and Rollman.[10] These on treatment with an excess of 20% alcoholic potassium hydroxide at room temperature give the diselenides as oils which soon solidify. The resulting solids are washed with water and recrystallized from methanol.

(2) Purified selenium is prepared from the above solution of potassium selenocyanate by the addition of an equal weight of chopped ice followed by an excess of cold, concentrated hydrochloric acid added with stirring in a well ventilated hood (hydrogen cyanide is evolved). By keeping the solution cold, the selenium deposits as a powder rather than as gummy lumps, and after washing with water until odorless and then with methanol, is dried at 110–130°. If the powder sinters during the drying process, it may be ground in a mortar. Although this process probably does not remove any tellurium originally present, it gives a sufficiently pure product for use in the preparation of diselenides. Using this purified selenium, selenophenols are prepared by the method of Foster[11] and without isolation are oxidized to diselenides by passage of oxygen (or air) through the reaction mixture.

Preparation of Unsymmetrical Selenides

(1) By Action of a Diselenide on a Grignard Reagent. A Grignard reagent is prepared in the usual manner from 0.1 g. atom of pure magnesium and 0.1 mole of the desired halide in a 200-ml., 3-necked flask. The diselenide is dissolved in anhydrous ether or benzene and added to the Grignard reagent. Since an excess of diselenide makes isolation of the selenide more difficult, it is best to use a slight excess of the Grignard reagent. As the diselenide solution is added, the deep orange color is discharged and heat is evolved. The reaction mixture is cooled in ice and poured into a 500-ml. separatory funnel containing 100 ml. of saturated, ice-cold ammonium chloride solution and shaken cautiously until the two layers are clear. The hydrolysis is not violent unless a large excess of the Grignard reagent remains. The aqueous layer is separated and extracted with 25 ml. of ether and the combined ether layers are then extracted with 100 ml. of 2 *N* sodium hydroxide in three portions to remove the selenophenol. The time from the start of the hydrolytic reaction to the completion of the base extraction should be as short as possible in order to minimize oxidation of the selenophenol. The solution from the base extractions may be acidified and oxidized if it is desired to recover the diselenide. The ether layer is dried and distilled, reduced pressure

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[1] J. D. McCullough, This Journal, **64**, 2672 (1942).

[2] McCullough and Eckerson, *ibid.*, **67**, 707 (1945).

[3] Keimatsu and Yokota, *C. A.*, **24**, 5291 (1930).

[4] Leicester and Bergstrom, This Journal, **51**, 3587 (1929).

[5] Behagel and Seibert, *Ber.*, **66**, 708 (1933).

[6] Gaythwaite, Kenyon and Phillips, *J. Chem. Soc.*, 2280 (1928).

[7] H. Wuyts, *Bull. soc. chim.*, **35**, 168 (1906).

[8] A. Schönberg and co-workers, *Ber.*, **66B**, 237 (1933).

[9] H. M. Leicester, This Journal, **60**, 619 (1938).

[10] Behagel and Rollman, *J. prakt. Chem.*, **123**, 336 (1929).

[11] D. G. Foster, "Organic Syntheses," vol. 24, p. 89.

being used during distillation of the selenide. The yields are approximately 80% with simple benzene derivatives.

(2) **By the Action of an Arylselenium Monobromide on a Mercury Diaryl.**—A solution containing 0.01 mole of arylselenium monobromide is prepared from 0.005 mole of bromine and 0.005 mole of the diaryldiselenide in 25–50-ml. of carbon tetrachloride. This solution is added slowly to 0.01 mole of the mercury diaryl contained in approximately 100 ml. of carbon tetrachloride, shaking the mixture frequently during the addition. Although the mercury diaryl does not dissolve completely in the quantity of solvent specified, this is immaterial since solution takes place as the reaction proceeds. The reaction is usually rapid but may be hastened by warming if desired. If the solution has a dark color after standing a few minutes, an excess of the bromide is indicated and a small amount of the mercury diaryl should be added until no more than a slight red or brown color remains. A nearly quantitative precipitation of arylmercuric bromide accompanies the reaction. After standing for about an hour, the solution is filtered and the filtrate distilled, using reduced pressure during distillation of the selenide. If the selenide is a solid, distillation is unnecessary, in which case the carbon tetrachloride is driven off and the solid is recrystallized from methanol. The yields are nearly quantitative and fall short of 100% only through losses in handling and purification.

Purification of Unsymmetrical Selenides.—Solid selenides are conveniently purified by recrystallization from methanol. Liquid selenides may be distilled at reduced pressure but purification is more conveniently accomplished by conversion to the dibromide, or, where this compound is unstable, to the dichloride, followed by recrystallization from carbon tetrachloride. Dibromides are reduced back to selenides by dissolving in acetone[12] followed by the addition of water after the solution has become colorless, causing the separation of the selenide as a colorless oil. Dichlorides are reduced by means of powdered zinc in carbon tetrachloride or by refluxing with aqueous sodium sulfite–sodium carbonate solution.

The dihalides of unsymmetrical selenides tend to be less stable, lower melting and more soluble than those of symmetrical selenides and show a greater tendency to form supersaturated solutions. A more difficult problem of isolation and purification is therefore presented.

The validity of the new methods was established through the synthesis of seven known and four new selenides. The known selenides included di-*p*-tolyl, 4-bromodiphenyl, 4-methyldiphenyl, 4-methoxydiphenyl, phenylbutyl, phenylbenzyl and di-α-naphthyl. These were identified by means of their melting points as well as by the melting points and equivalent weights[1] of their dihalides. The melting points agree with literature values within 1° in all cases except for 4-methyl-diphenylselenium dibromide where decomposition makes an accurate determination difficult. The equivalent weights show a maximum deviation of 1.1% in the case of the unstable phenylbutylselenium dibromide and a mean deviation of 0.4% from theoretical values. The new selenides include **4-chloro-4'-methyldiphenyl,** m. p. 72–3°, m. p. dibromide 120°; **3-chlorodiphenyl,** b. p. 200–205° (28 mm.), m. p. dichloride 102–104°; **2-phenyl-4'-methyldiphenyl,** m. p. 80°, dichloride decomposes with evolution of HCl at ~160° and **phenyl-α-naphthyl** selenide, b. p. 180° (1 mm.). The equivalent weights of the dihalides showed a maximum of 1.1% deviation in the case of the unstable phenyl-α-naphthylselenium dichloride and a mean deviation of 0.5%.

In a number of cases selenides were synthesized by use of both of the new methods and identity of products established by mixed melting points.

Summary

Two new methods for the synthesis of unsymmetrical selenides are described. One method involves the action of a diselenide on a Grignard reagent, the other interaction of an arylselenium monobromide with a mercury diaryl. The yields in both cases are for the most part quite good and the products easily isolated. The methods were validated by synthesis of eleven selenides including four new compounds for which physical constants are given.

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[12] H. M. Leicester, THIS JOURNAL, 57, 1901 (1935).

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Pyrolysis of Some Polyethylene Amines

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In the commercial preparation of ethylene diamine by such reactions as 1,2-dichloroethane and ammonia there are also formed many other compounds, including diethylenetriamine, triethylenetetramine, tetraethylenepentamine and other similar compounds of higher molecular weights. The lower members of this series are separated by distillation, leaving as a residue a mixture of high boiling amines, known as "amine residue." The work described in this article was undertaken for the purposes of determining whether it were possible to convert these higher amines into ethylenediamine by pyrolysis.

This "amine residue," obtained from the Carbide and Carbon Chemicals Corporation, and dried for twenty-four hours over fused potassium hydroxide, was used as the basic material for this investigation. By use of vacuum distillation, molecular distillation and fractional crystallization of the picrates, it was found that this mixture contained about 10% triethylenetetramine; about 25% tetraethylenepentamine and over 30% pentaethylenehexamine. The remaining constituents were unidentified.

Experimental

The results reported in this paper are those obtained by pyrolysis studies carried out with the "amine residue" in the apparatus shown in Fig. 1. The "amine residue" was heated in a 500-cc. flask (h) and the vapors flowed through a tube (i), 1.0 × 55 cm., wound with 24-gage resistance wire and with suitable asbestos insulation. The temperature of the vapors was measured with a 360° thermometer (c) placed in a 2.0 × 15 cm. tube (k) insulated with one inch asbestos pipe covering. The gases were cooled in passing through tube (j), 1.0 × 41.0 cm., on which the degree of insulation was varied to avoid flooding the fractionating column (d). This column, 2.0 × 72.0

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