

CXC.—*The Benzyl and Nitrobenzyl Selenosulphates and the Benzyl and Nitrobenzyl Diselenides.*

By THOMAS SLATER PRICE and LIONEL MANFRED JONES.

THE chief methods which have hitherto been used for the preparation of organic diselenides are: (a) Oxidation of the seleno-mercaptans; (b) action of potassium diselenide on the potassium alkyl sulphates; (c) treatment of the monoselenide with selenium; (d) action of sodium diselenide on the alkyl halides; (e) action of selenium on the Grignard compounds. In many cases diselenides are formed as by-products in the preparation of the seleno-mercaptans and monoselenides. (For literature see: Jackson, *Annalen*, 1875, **179**, 1; Chabrié, *Ann. Chim. Phys.*, 1890, [vi], **20**, 202; Taboury, *Ann. Chim. Phys.*, 1908, [viii], **15**, 1; Wuyts, *Bull. Soc. chim.*, 1909, [iv], **5**, 405; Tschugaeff, *Ber.*, 1909, **42**, 49; Doughty, *Amer. Chem. J.*, 1909, **41**, 326. These papers also give full references to earlier work.)

In a preliminary note (*Proc.*, 1908, **24**, 134) we have shown how the method employed by Price and Twiss (*Trans.*, 1907, **91**, 2021, and succeeding papers) for the preparation of disulphides could be extended to the preparation of diselenides. A solution of sodium selenosulphate was obtained by digesting selenium with a solution of sodium sulphite and filtering from the undissolved selenium. On adding this solution to an alcoholic solution of benzyl chloride, a turbid liquid was obtained, which, however, soon cleared when heated on a water-bath under reflux. After a short

time a small quantity of a yellow oil separated, which, after removal from the remainder of the liquid, solidified on cooling; this was proved to be benzyl diselenide. Further quantities of the diselenide could be obtained from the mother liquor, either by electrolysis in a divided cell, or by the addition of sodium carbonate.

In the course of further work, an attempt was made to extend the above method to the preparation of the nitrobenzyl diselenides. It was found, however, that the solution obtained on heating sodium selenosulphate with *p*-nitrobenzyl chloride was very unstable. After a very short time, decomposition took place with the separation of much selenium, and it was only with great difficulty that the diselenide could be isolated. Various changes in the method of procedure were tried, but without success. Even when the heating was stopped as soon as the contents of the flask had become clear, and the solution rapidly cooled, decomposition took place after a time. The difficulty was finally overcome by using potassium sulphite in place of sodium sulphite. Rathke (*J. pr. Chem.*, 1865, **95**, 8) found that potassium selenosulphate is more stable in solution than the corresponding sodium salt, and this is apparently true for the alkyl derivatives of these salts.

The method of procedure when potassium sulphite was used was similar to that already indicated with sodium sulphite. The use of this salt had the further result that the various potassium alkyl selenosulphates were readily isolated. When the turbid liquid, which resulted from mixing the solution of potassium selenosulphate and the alcoholic solution of the alkyl chloride, was heated over a flame under reflux, the contents of the flask cleared in two or three minutes, and, after a few minutes longer, a precipitate of the potassium alkyl selenosulphate began to form. The reaction between the potassium selenosulphate and the alkyl halide is complete in a very short time, and consequently the heating was not continued for longer than ten minutes.\* At the end of that time the contents of the flask were rapidly cooled, with the result that the precipitate of the alkyl selenosulphate became much more bulky—at all events, in the case of the nitrobenzyl derivatives. This precipitate always contained some diselenide mixed with it, especially in the case of the benzyl compound. In our preliminary note we stated that this was probably formed according to the equation:



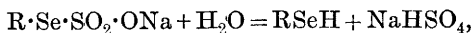
since some sulphur dioxide was evolved at the same time, but we are now of the opinion that this does not represent the true course

\* Prolonged heating, even with the potassium compounds, brought about decomposition with the liberation of selenium.

of the reaction. Bunte (*Ber.*, 1874, **7**, 646) and Purgotti (*Gazzetta*, 1890, **20**, 25) have shown that the alkyl thiosulphates undergo thermal decomposition with the formation of disulphides and dithionate, and it has also been noticed by one of us, in conjunction with Mr. D. F. Twiss, that solutions of sodium benzyl thiosulphate become cloudy on prolonged heating, the cloudiness being caused by the formation of benzyl disulphide. The selenium compounds are less stable than the corresponding sulphur compounds, and consequently thermal decomposition takes place to a greater extent, as represented by the equation:

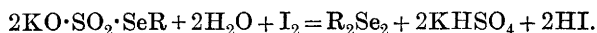


The evolution of sulphur dioxide was only noticed in the preparation of benzyl diselenide, and then only when sodium selenosulphate was used. Its formation was probably due to hydrolysis of the sodium benzyl selenosulphate by water,



and the subsequent action of the sodium hydrogen sulphate on the excess of sulphite present, or on the dithionate resulting from the thermal decomposition.

The mother liquor remaining after the precipitate of the potassium alkyl selenosulphate had been collected still contained considerable quantities of that compound. It was not recovered as such, but the diselenide was prepared from it in one of two ways. The most general method was by the action of iodine, dissolved either in alcohol or in potassium iodide solution, at the ordinary temperature. The reaction takes place very quickly, and proceeds quantitatively according to the equation:



The second method was by electrolytic reduction in a divided cell, after potassium hydrogen carbonate had been added to the solution (compare Price and Twiss, *Trans.*, 1907, **91**, 2021). It is noteworthy that not only could benzyl diselenide be prepared by the electrolytic method, but also *p*- and *m*-nitrobenzyl diselenides, whereas the corresponding nitrobenzyl disulphides could not be obtained in this way (compare *Trans.*, 1908, **93**, 1401). The *o*-nitrobenzyl diselenide could only be prepared by the iodine method; electrolysis led to the deposition of selenium, no diselenide being formed, probably because of steric hindrance, as was pointed out in the case of the corresponding *o*-disulphide.

All the selenium which passes into solution to form selenosulphate is recovered, either as the potassium alkyl selenosulphate or in the form of diselenide; that is, the yields obtained, as far as the

selenium is concerned, are quantitative. We have not investigated the respective yields of the alkyl selenosulphates and the diselenides.

The melting points of the diselenides prepared are given in the following table, and, for comparison, those of the corresponding disulphides:

	Diselenides.	Disulphides.
Benzyl.....	92—93°	71°.
<i>o</i> -Nitrobenzyl.....	103·5	109·5
<i>m</i> -Nitrobenzyl .....	106·0	103·0
<i>p</i> -Nitrobenzyl .....	107·5	126·5

It will be seen that in the case of the diselenides the substitution of the benzyl by the nitrobenzyl group has a considerably less effect than in the disulphides, and also that the influence of the position of the nitro-group is not so marked. Moreover, *m*-nitrobenzyl diselenide has a higher melting point than the corresponding ortho-compound, whereas in the case of the disulphides the order is reversed. It is also noteworthy that, although the substitution of sulphur by selenium raises the melting point of the benzyl compounds by 21—22°, the melting point of the *m*-nitrobenzyl compound is only raised by 3°, while the melting points of the *o*- and *p*-nitrobenzyl compounds are lowered by 6° and 19° respectively.

The potassium nitrobenzyl selenosulphates are much more easily prepared than potassium benzyl selenosulphate, since they are much less soluble in water. In this respect they are very similar to the corresponding thiosulphates (Price and Twiss, *Trans.*, 1908, **93**, 1401). All the selenosulphates and diselenides prepared are more or less slowly acted on by light, with the liberation of selenium. The benzyl compounds are the least, and the *m*-nitrobenzyl compounds the most stable.

#### EXPERIMENTAL.

Since the potassium nitrobenzyl selenosulphates were isolated before the corresponding benzyl compounds, they will be described first, together with the corresponding diselenides.

##### *Potassium p-Nitrobenzyl Selenosulphate*, $\text{KO} \cdot \text{SO}_2 \cdot \text{Se} \cdot \text{C}_7\text{H}_6 \cdot \text{NO}_2$ .

2·3 Grams of finely powdered selenium were boiled with a solution of 6 grams of potassium sulphite in 50 c.c. of water for three-quarters of an hour, and the hot solution filtered \* from the small amount of selenium remaining undissolved; 5 grams of *p*-nitrobenzyl

\* In most cases the filtrate remained clear on cooling to the ordinary temperature, but sometimes there was a very slight precipitate of selenium, which, however, did not affect the further treatment with the alkyl chloride, as it immediately disappeared on warming. When sodium sulphite was used in the place of potassium sulphite, much selenium was precipitated as soon as the solution was cooled.

chloride, dissolved in 50 c.c. of alcohol (95 per cent.), were then added, and the resulting turbid solution was heated over the free flame under reflux. The turbidity disappeared in a very short time, but after about five minutes a precipitate began to form. The heating was continued for ten minutes,\* and then the contents of the flask rapidly cooled. A copious precipitate, consisting chiefly of potassium *p*-nitrobenzyl selenosulphate, but containing also small quantities of *p*-nitrobenzyl diselenide and some potassium chloride, sulphate, and sulphite, was thereby produced. The inorganic salts were eliminated by recrystallising the precipitate several times from 95 per cent. alcohol. The traces of diselenide remaining were then removed by well shaking the recrystallised substance several times with ether, leaving the pure potassium *p*-nitrobenzyl selenosulphate.

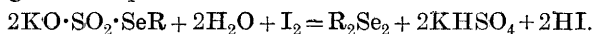
*Potassium p-nitrobenzyl selenosulphate* crystallises in plates, which are fairly soluble in water. In the bulk, the salt possesses a slight creamy tinge. On exposure to diffused daylight for some days, it is decomposed, with the liberation of selenium. The solution gives no precipitate with barium chloride; with sodium carbonate or sodium hydroxide, a yellow precipitate of the diselenide is produced. Hydrochloric acid gives a yellow precipitate, which consists of a mixture of the seleno-mercaptan and the diselenide; the precipitate forms slowly in the cold, but more quickly on warming. An alcoholic solution of iodine, or a solution of iodine in potassium iodide, gives an immediate precipitate of the diselenide.

The attempts to analyse this salt by estimating the potassium as sulphate were not very satisfactory. When heated very gently, either alone or after the addition of sulphuric acid, decomposition took place very rapidly with the liberation of selenium, and it was very difficult to regulate the decomposition so that no loss of salt occurred. It was found that the best method of procedure was to heat the salt alone until decomposition was complete, and then treat the residue with concentrated sulphuric acid. The potassium sulphate so obtained did not contain any selenium:

0.9144 gave 0.2342  $K_2SO_4$ .  $K=11.49$ .

$C_7H_6O_5NSKSe$  requires  $K=11.69$  per cent.

The most satisfactory method of analysis was one which depended on oxidation with iodine, which, as already indicated, takes place according to the equation:



The method of procedure was as follows. A weighed amount of the salt was dissolved in water and a slight excess of iodine in

\* In the first experiment in which potassium sulphite was used, the heating was continued for a longer time. After about twenty minutes the contents of the flask suddenly became red, owing to the copious deposition of selenium.

potassium iodide solution added. There was an immediate precipitate of the diselenide, and the end of the reaction was indicated by the rapid settling of the precipitate. The reaction was hastened by warming to a temperature of about  $45^{\circ}$  after the iodine had been added. The diselenide was collected, and well washed with hot water in order to remove all acid present. The iodine in the filtrate was then removed by careful addition of sodium thiosulphate, and the acid determined by titration with standard alkali. From the amount of acid liberated during the reaction, the percentage of potassium could be calculated. It was not found practicable to carry out the estimation by determining the amount of iodine used in the oxidation:

0.7531, after oxidation, required 33.03 c.c. of 0.1366*N*-NaOH.  
 $K = 11.71$ .

$C_7H_6O_5NSKSe$  requires  $K = 11.69$  per cent.

*p*-Nitrobenzyl Diselenide,  $(NO_2 \cdot C_6H_4 \cdot CH_2)_2Se_2$ .

This was prepared from the filtrate and mother liquors obtained in the preparation and recrystallisation of the potassium *p*-nitrobenzyl selenosulphate. An alcoholic solution of iodine was added until the colour of the iodine persisted, and then water, in order to precipitate the last traces of diselenide from the alcoholic solution. The diselenide was then recrystallised from alcohol, a drop of sulphurous acid being added to remove any iodine.

In one experiment the filtrate obtained in the preparation of potassium *p*-nitrobenzyl selenosulphate was electrolysed at the cathode in a divided cell (compare Price and Twiss, *Trans.*, 1907, **91**, 2021), after the addition of 6 grams of potassium hydrogen carbonate. A rotating cathode (area = 0.5 sq. dcm.) was used, and 0.25 ampere passed for one hour, and 0.5 ampere for another hour. A copious precipitate of the diselenide was formed. The filtrate from this precipitate, on standing in the dark overnight, gave a deposit of selenium. This was collected, and the filtrate again electrolysed, but there was only a further deposit of selenium.

It was also proved that the precipitate formed by the addition of sodium carbonate to an aqueous solution of potassium *p*-nitrobenzyl selenosulphate consists of the diselenide, but it is not as pure as that obtained by iodine oxidation or by electrolysis.

*p*-Nitrobenzyl diselenide, on recrystallisation from alcohol, gives a felted mass of canary-yellow crystals, which melt at  $107.5^{\circ}$ . On exposure to diffused daylight for some days it gradually turns red, owing to the liberation of selenium. With alcoholic sodium hydroxide it gives no immediate colour in the cold, but

a deep red colour on warming (compare the corresponding disulphide, *Trans.*, 1908, **93**, 1401).

The selenium was determined by the method of Frerichs (*Arch. Pharm.*, 1902, **240**, 656):

0.3218 required 29.63 c.c. *N*/10-potassium thiocyanate.  $\text{Se} = 36.46$ .

0.2051 gave 12.10 c.c.  $\text{N}_2$  (moist) at  $17^\circ$  and 739 mm.  $\text{N} = 6.62$ .

$\text{C}_{14}\text{H}_{12}\text{O}_4\text{N}_2\text{Se}_2$  requires  $\text{Se} = 36.79$ ;  $\text{N} = 6.51$  per cent.

#### *Potassium m-Nitrobenzyl Selenosulphate.*

This was prepared from *m*-nitrobenzyl chloride in a similar way to the corresponding para-compound, using the same quantities of reagents. It crystallises in colourless plates, which are fairly readily soluble in water, and are more readily obtained pure than the para-compound. Selenium is liberated on exposure to light:

0.5137, after oxidation, required 22.51 c.c. of 0.1366*N*-NaOH.

$\text{K} = 11.70$ .

$\text{C}_7\text{H}_6\text{O}_5\text{NSKSe}$  requires  $\text{K} = 11.69$  per cent.

#### *m-Nitrobenzyl Diselenide.*

This was obtained from the *m*-nitrobenzyl selenosulphate by oxidation with iodine, in a similar manner to that already described for the *p*-diselenide. It could also be prepared by electrolytic reduction of the selenosulphate. It crystallises from alcohol in flat needles, which possess only a very faint yellow tinge, and melt at  $106^\circ$ . It is much more stable towards diffused daylight than the *p*-diselenide, but on prolonged exposure it gradually acquires a red tinge. With alcoholic sodium hydroxide it gives a red colour on warming:

0.3050 required 28.55 c.c. *N*/10-potassium thiocyanate.  $\text{Se} = 37.08$ .

0.3868 gave 23.20 c.c.  $\text{N}_2$  (moist) at  $19.2^\circ$  and 734.9 mm.  $\text{N} = 6.62$ .

$\text{C}_{14}\text{H}_{12}\text{O}_4\text{N}_2\text{Se}_2$  requires  $\text{Se} = 36.79$ ;  $\text{N} = 6.51$  per cent.

#### *Potassium o-Nitrobenzyl Selenosulphate.*

This is prepared in a similar manner to the para- and meta-compounds, and possesses similar properties. It crystallises from alcohol in colourless plates:

0.4423, after oxidation, required 19.40 c.c. of 0.1366*N*-NaOH.

$\text{K} = 11.72$ .

$\text{C}_7\text{H}_6\text{O}_5\text{NSKSe}$  requires  $\text{K} = 11.69$  per cent.



*o*-Nitrobenzyl Diselenide.

This was prepared from the potassium *o*-nitrobenzyl selenosulphate by oxidation with iodine, exactly as described for the para- and meta-compounds. It could not be obtained by electrolytic reduction of the selenosulphate. It crystallises from alcohol in yellow plates, which melt at 103·5°. It is about as sensitive to light as the para-compound. With alcoholic sodium hydroxide, it gives a deep red colour on warming:

0·2877 required 32·15 c.c. *N*/10-potassium thiocyanate. Se=36·85.

0·2116 gave 12·30 c.c. N<sub>2</sub> (moist) at 20° and 756 mm. N=6·58.

C<sub>14</sub>H<sub>12</sub>O<sub>4</sub>N<sub>2</sub>Se<sub>2</sub> requires Se=36·79; N=6·51 per cent.

*Potassium Benzyl Selenosulphate*, KO·SO<sub>2</sub>·Se·CH<sub>2</sub>·C<sub>6</sub>H<sub>5</sub>.

The solution of this substance was prepared in a similar manner to that used for the nitrobenzyl compounds, the quantities taken being 3 grams of selenium, 8 grams of potassium sulphite, 40 c.c. of water, and 40 c.c. of alcohol. Owing to the ready solubility of the salt in water, however, the quantity of precipitate which separated on cooling was very small; also, since potassium benzyl selenosulphate is much less stable than the corresponding nitrobenzyl salts, the precipitate contained a large proportion of the diselenide. In order to remove the diselenide, the solution, together with the precipitate, was extracted with ether. The aqueous layer was then evaporated to dryness over concentrated sulphuric acid in a vacuum, and the potassium benzyl selenosulphate extracted from the residue by boiling with 95 per cent. alcohol. The crystals which separated from the alcoholic extract on cooling were, however, by no means pure. In the preparation of the potassium selenosulphate, some sulphite remains unacted on by the selenium, and this, to some extent, forms potassium benzylsulphonate with the benzyl chloride. Repeated crystallisation from alcohol is necessary to purify the benzyl selenosulphate from the benzyl sulphonate.

*Potassium benzyl selenosulphate* crystallises in colourless plates, which are very readily soluble in water. On exposure to light, decomposition readily takes place with liberation of selenium. The solution gives no precipitate with barium chloride. Oxidation with iodine gives the diselenide, but this reaction cannot be used for the analysis of the salt, since the diselenide does not settle readily, and excess of iodine seems to facilitate decomposition, with liberation of selenium. The best method of determining the percentage of potassium is to decompose the salt by gentle heat—the decomposition does not take place violently, as in the case of the



nitrobenzyl compounds—and then treat the residue with concentrated sulphuric acid. This method is also a good test of the purity of the salt. If it is quite pure, heating alone gives potassium sulphate, the weight of which is not altered by treatment with sulphuric acid, whereas, if potassium benzyldisulphonate is present, the residue left after heating contains potassium sulphite:

0.3024 gave 0.3189  $\text{CO}_2$  and 0.0764  $\text{H}_2\text{O}$ .  $\text{C}=28.76$ ;  $\text{H}=2.83$ .

0.5017 „ 0.1521  $\text{K}_2\text{SO}_4$ .  $\text{K}=13.60$ .

$\text{C}_7\text{H}_7\text{O}_3\text{SKSe}$  requires  $\text{C}=29.02$ ;  $\text{H}=2.44$ ;  $\text{K}=13.51$  per cent.

*Benzyl Diselenide,  $(\text{C}_6\text{H}_5\cdot\text{CH}_2)_2\text{Se}_2$ .*

This was prepared from potassium benzyl selenosulphate, either by oxidation with iodine, or by electrolytic reduction. For the first method, the alcoholic mother liquors obtained in the recrystallisation of the potassium benzyl selenosulphate were generally used. After excess of iodine had been added, the diselenide remaining in solution was precipitated by the addition of water. It was collected immediately and recrystallised from alcohol, since, as has already been pointed out, the presence of iodine seemed to facilitate the decomposition, with liberation of selenium. When recrystallising, a drop of sulphurous acid was added to remove any iodine present, and it was also necessary to wash the crystals well with water to remove any traces of hydriodic acid before they were dried.

For the electrolytic method, an aqueous solution of potassium benzyl selenosulphate was used, the method of procedure being similar to that described for *p*-nitrobenzyl diselenide. The strength of current was 0.25 to 0.5 ampere.

Benzyl diselenide crystallises from alcohol in yellow needles, which are slightly deeper in colour than those of *p*-nitrobenzyl diselenide, and melt at  $92-93^\circ$ . Jackson (*Annalen*, 1875, **179**, 1) describes the crystals as lustrous, yellow plates, melting at  $90^\circ$ . It is possible that the compound he obtained was not quite pure, since we have found that the slightly impure crystals have properties agreeing with those described by Jackson, even to the melting point. This is especially the case when the crystals are obtained from a concentrated alcoholic solution.

Benzyl diselenide is very sensitive to light as compared with the nitrobenzyl compounds. An exposure of an hour or so to diffused daylight turns it red:

0.2122 required 24.77 c.c. *N*/10-potassium thiocyanate.  $\text{Se}=46.2$ .

$\text{C}_{14}\text{H}_{14}\text{Se}_2$  requires  $\text{Se}=46.5$  per cent.

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CHEMICAL DEPARTMENT,  
MUNICIPAL TECHNICAL SCHOOL,  
BIRMINGHAM.

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