## 356. *The Nitration of Phenyl Selenocyanate.*

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IT was suggested by Challenger, Higginbottom, and Huntington (J., 1930, 26) that the *o* : *p*-ratio for the nitration of phenyl selenocyanate might be expected to be greater than that for phenyl thiocyanate (1 : 4), since rise in the atomic number of the halogens increases ortho-substitution (Lapworth and Robinson, *Mem. Manchester Lit. Phil. Soc.*, 1927—8, **72**, 49; *Ann. Reports*, 1928, 141).

This has now been found to be the case. At — 10°, a mixture of sulphuric acid (98%) and nitric acid (*d* 1·41) being used, after two hours the uncorrected *o* : *p*-ratio for phenyl selenocyanate is 25 : 75. This was determined from the m. p. of the mixture and comparison with a fusion curve obtained with mixtures of synthetic *o*- and *p*-nitrophenyl selenocyanates. Under these conditions the nitration is exceedingly clean, and no dinitration could be detected by analysis, molecular-weight determination, or fractional crystallisation. Comparison of the m. p.'s of mixtures, prepared synthetically, containing *o*-, *m*-, and *p*-nitrophenyl selenocyanates in known proportions, with those of the nitration mixture to which weighed quantities of these selenocyanates had been added indicated the absence of any appreciable *m*-nitrophenyl selenocyanate in the nitration mixture.

In no case at — 10° did the yields of mononitrophenyl selenocyanates from the nitration of phenyl selenocyanate exceed 88%. The loss is due to oxidation of both the phenyl selenocyanate and the mononitro-compounds to the corresponding seleninic acids, $R{\cdot}SeO_2H$.

The formation of these, which could not be prevented, was detected in the diluted spent acid by reduction with sulphur dioxide and separation of the precipitated mixture of diphenyl diselenide and dinitrodiphenyl diselenides by fractional crystallisation from alcohol.

In only one case was a seleninic acid actually isolated, *viz.*, the treatment of *p*-nitrophenyl selenocyanate (p. 1612) with sulphuric acid and nitric acid (*d* 1·485). The resulting *p*-nitrobenzeneseleninic acid was also obtained by Behaghel and Seibert (*Ber.*, 1933, **66**, 716) from the corresponding trihalide and water. One of us and Peters (J., 1928, 1364) observed similar oxidation of *p*-chloro-, *p*-bromo-, and *p*-thiocyano-phenyl selenocyanates and of *p*-tolyl selenocyanate.

The uncorrected value (25 : 75) of the *o* : *p*-ratio for the nitration of phenyl selenocyanate requires some adjustment, as the resulting nitrophenyl selenocyanates undergo coincident oxidation to the corresponding nitrobenzeneseleninic acids at different rates. The velocity constant calculated for the oxidation of the *o*-compound at —10° is approximately ten times that for the *p*-derivative. Accurate correction of the 25 : 75 ratio is impossible owing to the variable factors which influence the oxidation process. A sufficient approximation can, however, be obtained by determining the alteration in composition of the 25 : 75 mixture through contact with the mixed acids under, so far as possible, the same conditions as obtain in the nitration of phenyl selenocyanate. The necessary calculation can then be applied. Thus in Exp. 7, after two hours, 1 g. of the 25 : 75 mixture in sulphuric acid (98%, 5 c.c.) and nitric acid (*d* 1·41, 8 c.c.), which formed a saturated solution, gave a 92·5% yield of a 21 : 79 mixture. 0·0557 G. of the *o*- and 0·019 g. of the *p*-nitrophenyl selenocyanate had therefore been oxidised: the results in Exps. 6, 7, 8, and 15 are almost identical. As will be shown later, oxidation is limited to dissolved nitrophenyl selenocyanates. Consequently in a typical instance (Expt. 3, Table II) the calculated initial ratio becomes $(2{\cdot}2 \times 0{\cdot}25 + 0{\cdot}056/0{\cdot}925) : (2{\cdot}2 \times 0{\cdot}75 + 0{\cdot}019/0{\cdot}925) = 27 : 73$, which is probably as close an approximation as is practicable. The velocity constants, $k_o$, for the oxidation of *o*-nitrophenyl selenocyanate to the corresponding seleninic acid, $R{\cdot}SeO_2H$ (see p. 1613), from — 10° to + 10°, plotted against the corresponding temperatures, lie on a normal smooth curve, showing the absence of any marked secondary reactions.

The nitration process being accompanied by oxidation, it was of interest to determine whether this was preceded by or associated with hydrolysis under the influence of the sulphuric acid in the nitration mixture. It was shown by Behaghel and Rollmann (*Ber.*, 1929, **62**, 2696; see also *J. pr. Chem.*, 1929, **123**, 337) that the hydrolysis of selenocyanoacetic acid by acid or alkali follows the equation $2CO_2H{\cdot}CH_2{\cdot}SeCN + HOH = (CO_2H{\cdot}CH_2Se)_2 + HCN + HOCN$ and later (*Ber.*, 1932, **65**, 812) Behaghel and Seibert brought forward evidence to show that the hydrolysis of phenyl selenocyanate with alkali hydroxide takes a similar course, giving diselenide, cyanide, and cyanate. Although no diselenide was directly isolated in our experiments with a mixture of sulphuric and nitric acids and phenyl or the nitrophenyl selenocyanates, it appeared possible that this might have been formed first and undergone oxidation by the nitric acid to the seleninic acid. The effect of omitting the nitric acid was therefore studied.

In separate experiments, carried out at ordinary laboratory temperature with sulphuric acid alone, after three hours, a small amount of decomposition of the *o*-nitrophenyl selenocyanate was observed. The resulting nitrobenzeneseleninic acid was detected as the dinitro-diselenide after reduction with sulphur dioxide.

*p*-Nitrophenyl selenocyanate behaves differently. With sulphuric acid alone, no decomposition was detected at — 10°, but at 15° decomposition was extensive, producing a minimum yield of 50% of *pp'*-dinitrodiphenyl diselenide. The marked alteration in the ratio $k_o/k_p$ observed at — 5° shows that even at this temperature secondary reactions, presumably diselenide formation, followed by oxidation, have already begun to occur. The mechanism of this decomposition is under investigation.

It would therefore appear that, in the nitration experiments (1—8) and (13—15) with mixed acid at — 10°, diselenide formation by the sulphuric acid does not occur and the oxidation to seleninic acids is presumably direct. The oxidation of *p*-chloro- and *p*-bromophenyl selenocyanates to the corresponding seleninic acids by nitric acid can certainly occur in the absence of sulphuric acid (Challenger and Peters, *loc. cit.*). Substitution of nitric acid (*d* 1·485) for the corresponding quantity of nitric acid (*d* 1·41) produced with phenyl selenocyanate and its *o*- and *p*-nitro-derivatives the corresponding seleninic acids almost exclusively. Phenyl selenocyanate gave 2·9% of dinitro-compound. No evidence of dinitration was obtained for the mononitrophenyl selenocyanates.

## EXPERIMENTAL.

*Thermal Diagram for the Analysis of the Nitrated Products.*—The diagram was constructed from the observed m. p.'s of the following synthetic mixtures of pure *p*-nitrophenyl selenocyanate (m. p. 141·0° after ten recrystallisations from alcohol–acetone) and pure *o*-nitrophenyl selenocyanate (m. p. 144·0° after ten recrystallisations from alcohol–acetone); Challenger and Peters (J., 1928, 1369) give 143°; D.R.-P. 255,982 records 144—145°.

TABLE I.

| *p*-, % ... | 91·5 | 80·1 | 69·4 | 63·1 | 55·25 | 48·0 | 39·1 | 33·5 | 28·45 | 16·66 | 10·13 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| M. p. ... | 137·4° | 130·5° | 124·2° | 120·1° | 115·5° | 110·5°* | 118·4° | 123·1° | 126·2° | 133·1° | 138·5° |

* Eutectic.

*Nitrations of Phenyl Selenocyanate.*—2 G. of phenyl selenocyanate (b. p. 127°/17 mm. after four fractionations) (Behaghel and Seibert, *Ber.*, 1932, **65**, 815) were nitrated at various temperatures by slow addition to a mixture of 5 c.c. of 98% sulphuric acid and 8 c.c. of nitric acid (*d* 1·41). After 15 minutes a solid separated and the mixture slowly became pasty. After 2 hours the product was poured on ice, filtered, washed until the wash waters were neutral to litmus, dried, and weighed, and the m. p. determined. In Expt. 5A, the final dried product had a very faint odour of phenyl selenocyanate. This liquid compound, however, has a very intense odour, and minute traces only could have been present. After ultimate analysis, the product was treated with aqueous sodium bicarbonate, washed, and dried for 3 days in warm air. It was then odourless and was treated a second time with aqueous sodium bicarbonate (to remove any seleninic acids which might conceivably have arisen by atmospheric oxidation), washed, and dried in a vacuum desiccator. The m. p. 128·2° (Table II) was unchanged, and the bicarbonate extracts, which were colourless, gave no precipitate after acidification and treatment with sulphur dioxide, indicating absence of seleninic acids.

TABLE II.

| Expt. | Temp. | Yield, g. | Yield, %. | M. p. of product. | *p*-, %, in mixture. | Conditions. |
|---|---|---|---|---|---|---|
| 1 | −5° to −2° | 1·48 | 60·0 | 137·4° | 91·5 | Nitric acid added to phenyl selenocyanate dissolved in sulphuric acid : reaction difficult to control. |
| 2 | −10 to 0 | 1·36 | 54·6 | 135·6 | 88·5 | |
| 3 | −10 | 2·20 | 88·2 | 128·4 | 75 | Phenyl selenocyanate added to mixed acids. |
| 4 | −10 | 2·06 | 83·0 | 128·3 | 75 | ,, |
| 5 | −10 | 4·41 | 88·4 | 128·3 | 75 | ,, (double quantities) |
| 5A | −12 to −15 | 4·40 | 88·3 | 128·2 | 75 | ,, ,, ,, |

Fractional crystallisation from alcohol–acetone of the 75 : 25 nitration product showed no evidence of the presence of 2 : 4-dinitrophenyl selenocyanate, or of the very sparingly soluble and high-melting dinitrodiphenyl diselenides. Analysis and mol.-wt. determination confirmed this conclusion [Found : C, 37·0; H, 1·8; N, 12·2; *M* (camphor), 210. Calc. for $C_7H_4O_2N_2Se$ : C, 37·0; H, 1·8; N, 12·3%; *M*, 227]. The presence of diphenyl diselenide is also excluded by analysis : this would, moreover, almost certainly have been oxidised to benzeneseleninic acid during the nitration and removed in the spent acid. The absence of any appreciable meta-nitration was shown in the following way : It was found that small amounts of *m*-nitrophenyl selenocyanate could replace the *o*- or *p*-compound on the *p*- or *o*-side respectively of the *o*-*p* m. p. curve. Thus :

(1) 0·0012 g. *m* + 0·0036 g. *o* + 0·0108 g. *p* (7·7 : 23·1 : 69·2), m. p. 124·5°. This point on the *o*-*p* constructed m. p. curve corresponds to a 30·6 : 69·4 mixture.

(2) 0·0017 g. *m* + 0·022 g. *o* + 0·0034 g. *p* (6·3 : 81·2 : 12·5), m. p. 131·5°, corresponding to a 80·8 : 19·2 mixture on the *o*-*p* m. p. curve.

Consequently, (1) various weights of the *o*-nitro-compound were added to the nitration mixture in order to form products lying on both sides of the *o*-*p* curve, and their m. p.'s were determined. In all cases they agreed with those deduced from the thermal diagram. Thus :

(a) 0·0088 g. nitro-product + 0·0067 g. *o*-nitro-selenocyanate. Total % of *o* = 57·4; m. p. 115·3°; deduced from curve, 115·5°.

(b) 0·0048 g. nitro-product + 0·0078 g. *o*-nitro-selenocyanate. Total % of *o* = 71·4; m. p. 125·8°; deduced from curve, 126·1°.

(c) 0·0080 g. nitro-product + 0·0032 g. *p*-nitro-selenocyanate. Total % of *o* = 17·8; m. p. 132·1°; deduced from curve, 132·2°.

(2) *m*-Nitrophenyl selenocyanate (m. p. 65·5°) was added to a synthetic mixture of the *o*- and *p*-compounds, the latter being present in the eutectic ratio (52 : 48) as indicated on the *o*-*p* curve; the m. p. of the resulting mixture was determined and compared with that of a mixture of *m*- together with a nitration mixture to which *o*- had been added in amount calculated to bring an assumed 25 : 75 *o*-*p* proportion to the eutectic ratio. Thus :

(a) 0·0102 g. *o* + 0·0093 g. *p* + 0·0016 g. *m* $(o : p : m = \underbrace{48\cdot3 : 44\cdot1}_{\text{eutectic ratio}} : 7\cdot6)$; m. p. 105·8°.

(b) 0·016 g. nitration mixture + 0·009 g. *o* + 0·002 g. *m* $(o : p : m = (?)\underbrace{48\cdot2 : 44\cdot4} : 7\cdot4)$; m. p. 105·9°.

The filtered diluted spent acids from experiments 1—5 were treated with sulphur dioxide. Crystallisation of the resulting precipitates from alcohol yielded diphenyl diselenide, m. p. 62·5°, and small quantities of a less soluble mixture of nitrated diphenyl diselenides. These products arose from reduction of the corresponding seleninic acids.

*Nitration of Phenyl Selenocyanate and Simultaneous Oxidation.*—Phenyl selenocyanate (4·0 g.), when nitrated at − 10° with sulphuric acid (10 c.c.) and nitric acid (*d* 1·485; 12·1 c.c.), gave no mononitro-selenocyanate. The products consisted of 3·016 g. of *p*-nitrobenzeneseleninic acid (Behaghel and Seibert, *Ber.*, 1933, **66**, 716), m. p. 214° (decomp.) after crystallisation from boiling water (yield, 73%), and 0·142 g. of 2 : 4-dinitrophenyl selenocyanate (separated by treatment of the crude product with sodium bicarbonate solution), which, after crystallisation from alcohol, melted at 168·3° and did not depress the m. p. (168·3°) of an authentic synthesised sample; yield, 2·9%. Fromm and Martin (*Annalen*, 1913, **401**, 181) give m. p. 163°.

The seleninic acid was further identified by treating its boiling aqueous solution with sulphur dioxide and analysing the precipitated *pp*′-dinitrodiphenyl diselenide (Found : C, 36·0; H, 2·0; N, 7·2. Calc. : C, 35·8; H, 2·0; N, 7·0%). After crystallisation from glacial acetic acid, this dinitro-diselenide decrepitated at 137·5° and melted at 183°. Behaghel and Seibert (*Ber.*, 1933, **66**, 713) give m. p. 177° for an unanalysed specimen.

Benzenesulphinic acid and also *p*-nitro-, *p*-chloro-, and *p*-bromo-benzeneseleninic acids give with a cold mixture of diphenylamine and sulphuric acid an intense blue colour resembling that produced by nitric acid. This property of seleninic acids does not appear to have been recorded, although it is well known that various oxidising agents, including selenates and chlorates, can replace nitric acid in this reaction.

*Further Treatment of the Nitration Products of Phenyl Selenocyanate* (o : p = 25 : 75) *with Mixed Acids.*—1 G. of the 75 : 25 mixture of mononitrophenyl selenocyanates was treated with 5 c.c. of sulphuric acid (98%) and 8 c.c. of nitric acid (*d* 1·41) for various times at different temperatures. The products were poured on ice, and the yields and compositions (Table III) determined as before.

TABLE III.

| Expt. | Time, hrs. | Temp. | Recovered yield, %. | M. p. | *p*-, %, in product. | Expt. | Time, hrs. | Temp. | Recovered yield, %. | M. p. | *p*-, %, in product. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 2 | −10° | 92·75 | 130·3° | 79 | 11 | 2 | 5° | 58·7 | 134·65° | 86·4 |
| 7 | — | — | 92·5 | 130·3 | 79 | 12 | — | 10 | 48·2 | 135·7 | 88·4 |
| 8* | — | — | 92·35 | 130·3 | 79 | 13 | 0·5 | −10 | 98·1 | 128·6 | 76 |
| 9 | — | − 5 | 86·10 | 132·0 | 81·8 | 14 | 1·0 | — | 96·27 | 129·3 | 77 |
| 10 | — | 0 | 68·7 | 131·8 | 81·4 | 15 | 1·5 | — | 94·38 | 129·8 | 78 |

* After 6 weeks' standing with the diluted nitration acid after pouring on ice.

At − 10° the solubility of the 75 : 25 mixture in the above quantity of nitrating acid was approximately 1·0 g. 2·0 G. of this mixture were treated with the same quantity of acid at − 10° for 2 hours. The amount recovered was 1·924 g., m. p. 129·3° (77% *p*-), *i.e.*, 0·019 g.

of *p*- and 0·057 g. of *o*- had disappeared. Since these are the same quantities as disappeared in the treatment of 1 g. of the mixture in Expt. 7, Table IV (0·019 g. and 0·056 g. respectively), it follows that the undissolved nitro-compounds had not been affected by the nitrating acid. (Neither were they affected by prolonged contact with diluted spent acid; Expt. 8 in Table III.) Oxidation is therefore limited to the homogeneous liquid phase, and, in view of the large excess of nitrating agent, velocity constants for the oxidation of *p*- and *o*-nitrophenyl selenocyanates, under the conditions above quoted, were calculated on the basis of a unimolecular equation, $k = 1/t. \log a/(a - x)$. Table IV shows the results obtained.

TABLE IV.

| Expt. | Time, hrs. | Temp. | Amount of *p*- (g.) at beginning. | at end. | $k_p$. | Amount of *o*- (g.) at beginning. | at end. | $k_o$. | $k_o/k_p$. |
|---|---|---|---|---|---|---|---|---|---|
| 6 | 2 | −10° | 0·75 | 0·7326 | 0·0051 | 0·25 | 0·1947 | 0·054 | 10·6 |
| 7 | — | — | ,, | 0·731 | 0·0056 | ,, | 0·1943 | 0·055 | 9·8 |
| 8 | — | — | ,, | 0·7295 | 0·006 | ,, | 0·1939 | 0·055 | 9·2 |
| 9 | — | − 5 | ,, | 0·7033 | 0·014 | ,, | 0·1577 | 0·100 | 7·1 |
| 10 | — | 0 | ,, | 0·5593 | 0·0637 | ,, | 0·1277 | 0·146 | 2·3 |
| 11 | — | 5 | ,, | 0·5071 | 0·085 | ,, | 0·0798 | 0·248 | 2·9 |
| 12 | — | 10 | ,, | 0·4261 | 0·123 | ,, | 0·0559 | 0·325 | 2·6 |
| 13 | 0·5 | −10 | ,, | 0·7457 | 0·0050 | ,, | 0·2355 | 0·051 | 10·2 |
| 14 | 1·0 | — | ,, | 0·7413 | 0·0051 | ,, | 0·2214 | 0·053 | 10·3 |
| 15 | 1·5 | — | ,, | 0·7362 | 0·0054 | ,, | 0·2076 | 0·053 | 9·9 |

*Treatment of Synthetic Nitrophenyl Selenocyanates with Sulphuric Acid and Nitric Acid* (d 1·485).—p-*Nitrophenyl selenocyanate.* This compound (0·3 g.) was added to a mixture of sulphuric acid (98%, 5 c.c.) and nitric acid (*d* 1·485, 6 c.c.) at − 15°. After 2 hours the product was poured on 100 g. of ice, filtered, washed, and dried. The *p*-nitrobenzeneseleninic acid obtained, 0·215 g. (69·5% yield), had m. p. 214° (decomp.) after two crystallisations from boiling water. The acid filtrate, after passage of sulphur dioxide, gave 0·06 g. of *pp*′-dinitrodiphenyl diselenide (yield, 22·0%), m. p. 183° after one crystallisation from acetic acid. Total recovery, 91·5%. The filtrate from the sulphur dioxide treatment was colourless and deposited no tetranitrodiphenyl diselenide, though this does not necessarily exclude the occurrence of some dinitration (see below).

o-*Nitrophenyl selenocyanate.* The compound (0·5 g.), on similar treatment, gave no precipitate with ice owing to the solubility of the corresponding seleninic acid. Treatment of the diluted liquid with sulphur dioxide gave 0·436 g. of *oo*′-dinitrodiphenyl diselenide (yield, 98·4%), m. p. 211°, which after one crystallisation from glacial acetic acid melted at 215° (Bauer, *Ber.*, 1913, **46**, 95, gives 209°). No evidence of dinitration was obtained.

2 : 4-*Dinitrophenyl selenocyanate.* The dinitro-compound (0·5 g.) was treated as before. The dinitro-seleninic acid was completely soluble, and was only very slowly reduced to the corresponding diselenide, of which but 0·223 g. (yield, 47·5%) was obtained after 5 days' standing : m. p. (crude material) 262° (decomp.). Fromm and Martin (*loc. cit.*, p. 182) give m. p. 264°.

*Action of Sulphuric Acid on the Mononitrophenyl Selenocyanates.*—0·3 G. of *o*-nitrophenyl selenocyanate was treated with 10 c.c. of sulphuric acid at − 10° for 3 hours, poured on 100 g. of ice, filtered, washed, and dried. The m. p. was 144°, and the yield, 0·297 g. (99%). The compound was therefore unchanged. The filtrate showed only traces of diselenide on treatment with sulphur dioxide. Recovery under similar conditions, but immediately after solution in the sulphuric acid, gave the same result. Under the same conditions the pure *p*-nitro-compound showed an exactly similar stability. The same experiment was then repeated with the *o*-nitro-derivative at laboratory temperature. Slight deepening in colour was observed but no effervescence, and no odour : yield, 0·275 g. (92%), m. p. 143·7°. The product was completely soluble in 10 c.c. of cold absolute alcohol (absence of diselenide). The acid filtrate on treatment with sulphur dioxide gave 0·006 g. of *oo*′-dinitrodiphenyl diselenide (2% yield) ; m. p. of crude material 213°.

*Abnormal Behaviour of* p-*Nitrophenyl Selenocyanate.*—The same experiment was repeated with 0·5 g. of the *p*-nitro-compound, the same quantity of sulphuric acid being used at laboratory temperature. The mixture developed a deep red colour in ½ hour, and effervescence occurred on occasional stirring. After 3 hours the mixture was poured on ice; yield of solid, 0·392 g., m. p. 166°. This was extracted with cold aqueous sodium bicarbonate and filtered. The filtrate, after addition of hydrochloric acid and standing for 3 days, deposited white needles, too small in amount either to weigh or to identify, which gave a strong orange colour with alcoholic potassium hydroxide (possibly *p*-nitrobenzeneselenenic acid, R·SeOH, as the corresponding *p*-seleninic acid gives no colour with alcoholic potassium hydroxide). The residue from the sodium bicarbonate treatment, after repeated extraction with cold alcohol–acetone, gave 0·221 g. of *pp'*-dinitrodiphenyl diselenide, m. p. 183° (50% yield).

*Behaviour of the* 25 : 75 *Mixture.*—Nitrogen, free from carbon dioxide, was passed through 4·0 g. of the 25 : 75 mixture in 50 c.c. of sulphuric acid at laboratory temperature for 6 hours, and was then bubbled through 50% aqueous potassium hydroxide. The issuing gas was passed over iodine pentoxide at 160° into aqueous potassium iodide to detect any carbon monoxide. The mixture developed a deep brownish-red colour in 5 minutes and the potassium hydroxide solution was found to contain much carbonate and sulphite. The diluted acid liquor contained ammonium sulphate and the precipitated solid yielded on extraction with alcohol–acetone *pp'*-dinitrodiphenyl diselenide, a mixture of the *o*- and *p*-nitrophenyl selenocyanates remaining. Titration of the liberated iodine indicated a yield of carbon monoxide equal to 0·15% of the *p*-nitrophenyl selenocyanate in the original mixture.

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