CLXXXII.—*The Nitration of Aromatic Thiocyanates and Selenocyanates.*

By Frederick Challenger and Arnold Thornton Peters.

In a previous communication by one of us and Collins (J., 1924, **125**, 1377) it was shown by the nitration of phenyl thiocyanate that the thiocyano-group possesses a strong para-directing influence, relatively very small amounts of *o*-nitrophenyl thiocyanate being formed. When the para-position is occupied by (*a*) chlorine or (*b*) bromine, the nitro-group enters in the ortho-position to ·SCN. In case (*a*), the product was homogeneous, whereas in (*b*) traces of a second nitro-compound appeared to be present. With *p*-iodophenyl thiocyanate and *p*-bromoiodobenzene replacement of iodine by the nitro-group occurs. Mayes and Turner (this vol., p. 691) have observed a similar effect.

On nitration of *p*-tolyl thiocyanate, however, two isomeric mononitro-compounds are formed, the principal product containing the nitro-group in the ortho-position to methyl. In this case, the course of the reaction appears to be determined chiefly by the methyl group.

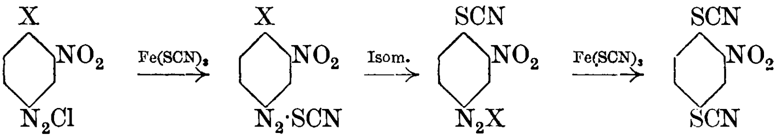
It was therefore of interest to ascertain the behaviour of *o*-tolyl thiocyanate (Thurnauer, *Ber.*, 1890, **23**, 771) on nitration, and it has now been shown that the principal product is 5-*nitro*-o-*tolyl thiocyanate* and a much smaller amount of the 4-*nitro*-derivative is produced. The influence of the thiocyano-group is therefore predominant. Here, as in all other cases described in this communication, the products of nitration were identified by direct comparison with authentic thiocyanates or selenocyanates obtained by the diazo-reaction.

In a later communication, it is hoped to discuss more fully the differing behaviour of the *o*- and *p*-tolyl thiocyanates, and Miss C. Higginbottom, B.Sc., is, in this connexion, studying the nitration of the *o*-halogenophenyl thiocyanates.

When 4-bromo (or chloro)-3-nitroaniline is diazotised and treated with ferric thiocyanate or with potassium cuprous thiocyanate, 4-*bromo*-3-*nitrophenyl thiocyanate* and 4-*chloro*-3-*nitrophenyl thiocyanate* are obtained. A large quantity of *nitro*-p-*dithiocyanobenzene* is also produced in each case, a halogen atom being eliminated. This has been identified by direct comparison with the product obtained (1) by nitration of the *p*-dithiocyanate and (2) from diazotised 2-nitro-4-thiocyanoaniline.

It was shown by Hantzsch and Hirsch (*Ber.*, 1896, **29**, 947; 1898, **31**, 1253) that the *p*-chloro- and *p*-bromo-benzenediazonium thiocyanates readily isomerise, usually in presence of acid, giving the *p*-thiocyanobenzenediazonium chloride or bromide. Similarly, 2 : 4-dibromobenzenediazonium chloride gives rise to a mixture of chlorobromo- and dichloro-benzenediazonium bromides (Hantzsch, *Ber.*, 1897, **30**, 2334).

The replacement of chlorine or bromine by thiocyanogen with production of a nitrodithiocyanobenzene probably proceeds in an analogous manner.



The formation of *p*-dithiocyanobenzene has not yet been observed during the preparation of *p*-chloro- and *p*-bromo-phenyl thiocyanates, although from the work of Hantzsch and Hirsch some dithiocyanate might be expected. The abnormal course of the Sandmeyer reaction with diazotised 4-chloro (or bromo)-3-nitroaniline and a thiocyanate is probably conditioned by the reactivity of the halogen atom in presence of the *o*-nitro-group, since with 4-bromo-2-nitroaniline the reaction proceeds normally (Challenger and Collins, J., 1924, **125**, 1379).

No abnormality could be detected when 4-bromo-3-nitroaniline was diazotised and treated with cuprous chloride, the sole product of the reaction apart from a trace of a high-melting solid being 4-chloro-1-bromo-2-nitrobenzene, m. p. 69—70° (Holleman, *Rec. trav. chim.*, 1915, **34**, 208, gives m. p. 70°). Nitro-*p*-dichlorobenzene could not be detected.

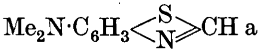
2-Nitro-4-thiocyanoaniline was obtained by nitration of *p*-thiocyanoacetanilide prepared by acetylation of the corresponding amine (Soderbäck, *Annalen*, 1919, **419**, 271). Its structure was proved by diazotisation and elimination of the diazo-group giving *m*-nitrophenyl thiocyanate. Replacement of the amino-group by chlorine, bromine, or selenocyanogen gives 4-*chloro*-3-*nitrophenyl thiocyanate*, 4-*bromo*-3-*nitrophenyl thiocyanate*, and 3-*nitro*-4-*selenocyanophenyl thiocyanate*, which were required as reference compounds for orientation purposes. p-*Dithiocyanobenzene* and p-*thiocyanoselenocyanobenzene* have been prepared from diazotised *p*-thiocyanoaniline.

The orienting effect of the selenocyano-group has also been investigated. *Phenyl selenocyanate*, which has not previously been described, gives on nitration principally the para-derivative, but some *o*-nitrophenyl selenocyanate is also obtained.

A comparison of the relative orienting effects of SeCN and the halogens and of SeCN and SCN has been attempted. This has, however, only been partly successful, since in many cases, even under the most varied conditions, the nitration of halogenated phenyl selenocyanates and of thiocyanoselenocyanobenzene leads to the production of aromatic seleninic acids, $R{\cdot}SeO_2H$, some of which have recently been obtained by Porritt (J., 1927, 27), using a different method. The nitration of *p*-tolyl selenocyanate (Challenger, Peters, and Halévy, J., 1926, 1654) with nitric acid (*d* 1·5) at −10° proceeds normally, giving as principal product 2-*nitro*-p-*tolyl thiocyanate*, m. p. 69°, the isomeric 3-*nitro*-derivative, m. p. 150°, being obtained in much smaller amount. This recalls the nitration of *p*-tolyl thiocyanate where the lower-melting 2-nitro-derivative predominates. When the nitration is conducted with sulphuric acid and nitric acid (*d* 1·41) at 3°, a mixture of di-2-nitro-*p*-tolyl diselenide and 2-nitro-*p*-tolueneseleninic acid is obtained. These are mutually interconvertible by oxidation and reduction. The position of the nitro-group in the diselenide was proved by its formation when synthetic 2-nitro-*p*-tolyl selenocyanate was treated with aqueous potassium hydroxide. When di-*p*-tolyl diselenide is warmed with nitric acid (*d* 1·41), *p*-tolueneseleninic acid is produced. This was obtained by Porritt by the oxidation of *p*-tolylselenoglycollic acid, $CH_3{\cdot}C_6H_4{\cdot}Se{\cdot}CH_2{\cdot}CO_2H$, with hydrogen peroxide.

When *p*-chlorophenyl selenocyanate is nitrated with nitric (*d* 1·41), and sulphuric acids below 3°, a mixture of di-*p*-chlorophenyl diselenide (Taboury, *Bull. Soc. chim.*, 1906, **35**, 673) and *p*-chlorobenzeneseleninic acid (Porritt, *loc. cit.*; Morgan and Elliot, P., 1914, 248) is produced. With nitric acid (*d* 1·5) at $-25°$ or $-10°$, a mixture of the seleninic acid and of 4-*chloro*-2-*nitrophenyl selenocyanate* is obtained, the acid predominating. No trace of a derivative containing a nitro-group in position 3 could be detected. The course of the nitration is therefore again analogous to that observed with the corresponding thiocyanate. On treatment of *p*-bromophenyl selenocyanate with nitric acid under the most varied conditions, only *p*-bromobenzeneseleninic acid could be isolated (Porritt, *loc. cit.*). It was characterised by reduction to the diselenide. The crude seleninic acid gives no purple colour with alcoholic alkali, indicating the absence of even traces of 4-bromo-2-nitrophenyl selenocyanate.

Treatment of *p*-thiocyanoselenocyanobenzene with nitric acid (*d* 1·41) and sulphuric acid at 3° or with nitric acid (*d* 1·5) at $-5°$ gives rise almost exclusively to p-*thiocyanobenezeneseleninic acid.* Traces of a second product containing sulphur, selenium, and nitrogen were once observed, but could not again be isolated.

Marsh (J., 1927, 3164) has shown that by the action of potassium thiocyanate and hydrogen peroxide on dimethylaniline in glacial acetic acid a product, m. p. 73°, is obtained which is identical with that obtained by Soderbäck (*Annalen*, 1919, **419**, 275) from an ethereal solution of thiocyanogen and dimethylaniline, and considered by him to be *p*-thiocyanodimethylaniline. Marsh suggests that this compound is probably not a true thiocyanate, but may have the constitution  $Me_2N{\cdot}C_6H_3{<}\genfrac{}{}{0pt}{}{S}{N}{>}CH$ and be identical with the benzthiazole derivative obtained by Schmidt (*Ber.*, 1906, **39**, 2409). We find, however, that with alcoholic potassium hydrosulphide it behaves normally, giving potassium thiocyanate, and that it may be obtained by heating *p*-thiocyanoaniline with excess of methyl iodide and liberation of the base with sodium bicarbonate (m. p. and mixed m. p. with Marsh's compound, 73°). The results of one of us and Collins (*loc. cit.*), of Dienske (*Rec. trav. chim.*, 1927, **46**, 154), and those described in this communication leave no room for doubt as to the constitution of *p*-thiocyanoaniline, which may also be obtained from aniline by Marsh's method. We have, however, prepared Schmidt's dimethylaminobenzthiazole (m. p. 73—74°) and find that it depresses the m. p. (73°) of Marsh's dimethylaniline derivative to 52°. There can therefore be no doubt that the compound obtained by Soderbäck and by Marsh is *p*-thiocyanodimethylaniline.

EXPERIMENTAL.

Nitration of o-*Tolyl Thiocyanate*.—The thiocyanate (15 g.) was slowly stirred into a mixture of nitric acid (*d* 1·41; 55 c.c.) and sulphuric acid (55 c.c.) at 3—8°, which after 3 hours was poured on ice, and the solid separated. Four crystallisations from alcohol gave white needles, m. p. 117·5—118·5°, not depressing the m. p. of 5-*nitro*-o-*tolyl thiocyanate* obtained from the corresponding nitro-*o*-toluidine by the Sandmeyer reaction. These formed the bulk of the nitration product (Found: S, 16·2. $C_8H_6O_2N_2S$ requires S, 16·5%). The mother-liquors deposited an oil which slowly solidified, and on recrystallisation white needles, m. p. 70—71°, were finally obtained. These did not depress the m. p. (70—70·5°) of 4-*nitro*-o-*tolyl thiocyanate* obtained by the Sandmeyer reaction.

Synthesis of the Isomeric Nitro-o-*tolyl Thiocyanates*.—(a) 5-*Nitro*-o-*tolyl thiocyanate*. 5-Nitro-*o*-toluidine (6 g.) in 60 c.c. of dilute sulphuric acid (1 : 5) was diazotised at 6° with 2·75 g. of sodium nitrite in 5 c.c. of water and added to a cold mixture of cuprous thiocyanate (10·8 g.) and potassium thiocyanate (5 g.) in the minimum of water. After 12 hours, the mixture was warmed at 100°; the precipitate was extracted with alcohol and after treatment with charcoal yielded colourless needles, m. p. 117·5—119°.

(b) 4-*Nitro*-o-*tolyl thiocyanate* was similarly prepared from the corresponding nitrotoluidine. It forms colourless needles, m. p. 70—70·5°, from light petroleum (Found: S, 16·2. $C_8H_6O_2N_2S$ requires S, 16·5%). The presence of the thiocyano-radical was proved by the formation of a mercaptan and potassium thiocyanate when the compound was boiled with alcoholic potassium hydrosulphide (Challenger and Collins, J., 1924, **125**, 1379).

In (a) and (b) the yields of nitro-thiocyanates are about 80%.

Preparation and Nitration of Phenyl Selenocyanate.—Aniline (9·1 g.) in dilute sulphuric acid (1 : 4) was diazotised at 3° with sodium nitrite (9·5 g.). The solution, made neutral to Congo paper with sodium acetate, was added to cold aqueous potassium selenocyanate (22 g.). The odour of an aryl selenocyanate was at once produced and after 15 hours steam distillation gave a pale yellow oil. After being dried with calcium chloride, this boiled at 134°/10 mm. and at about 250° (decomp.) at the ordinary pressure (yield, about 50%) (Found: N, 8·0; Se, 43·0, 43·0. C_7H_5NSe requires N, 7·7; Se, 43·4%). The selenocyanate (2 g.) was dissolved in nitric acid (*d* 1·5; 7 c.c.) at −5° and after 2 hours the mixture was poured on ice. The resulting solid (2·3 g.; m. p. 105°) was fractionated from alcohol, giving white, glistening plates of *p*-nitrophenyl selenocyanate, m. p. 141°, which developed a red colour with alcoholic potassium hydroxide and did not depress the m. p. of an authentic specimen obtained from *p*-nitroaniline (Bauer, *Ber.*, 1913, **46**, 92). The final mother-liquors yielded a relatively very small amount of *o*-nitrophenyl selenocyanate, m. p. 142—143°, not depressing the m. p. of a synthetic specimen (m. p. 143°) prepared from *o*-nitroaniline. It gave a strong purple colour with alcoholic potassium hydroxide (Bauer), which we find to be characteristic of selenocyanates containing an *o*-nitro-group. Bauer (*loc. cit.*) gives the m. p.'s of the *p*- and *o*-derivatives as 135° and 142°, respectively.

Pyman (J., 1919, **115**, 166) reduced *m*-nitrophenyl selenocyanate to the diamino-diselenide without giving details of the selenocyanate. As this compound is not mentioned elsewhere in the literature, we have prepared it from *m*-nitroaniline (see p. 1374). On crystallisation from light petroleum or from acetone–light petroleum it forms almost colourless plates, m. p. 65° (Found: N, 12·25. Calc. for $C_7H_4O_2N_2Se$: N, 12·3%).

Nitration of p-*Tolyl Selenocyanate.*—The selenocyanate (9 g.) was treated with nitric acid (*d* 1·41; 30 c.c.) and sulphuric acid (32 c.c.) at 3°, and after remaining for 4 hours at room temperature the mixture was poured on ice (100 g.). The pale yellow solid (12·5 g.) obtained, on fractionation from acetone–light petroleum, gave (A) white crystals, m. p. 151°, and (B) yellow crystals, m. p. 69°, which formed the bulk of the product. (A) was faintly acid and dissolved with effervescence in sodium bicarbonate solution, from which a silver salt could be precipitated. Analysis showed (A) to be 2-*nitro*-p-*tolueneseleninic acid* (Found: Se, 32·2, 31·8. $C_7H_7O_4NSe$ requires Se, 31·9%). Reduction with zinc and hydrochloric acid gave a yellow solid, m. p. 69° (from light petroleum), not depressing the m. p. of (B) obtained as above, nor that of the synthetic *di*-2-*nitro*-p-*tolyl diselenide* (m. p. 69°) obtained by the action of potassium hydroxide on the corresponding synthetic selenocyanate prepared by the diazo-reaction (see p. 1374) (Found for the synthetic diselenide: Se, 36·7, 36·6. $C_{14}H_{12}O_4N_2Se_2$ requires Se, 36·9%).

(B) was insoluble in sodium bicarbonate solution and unaffected by aqueous alkali and was obviously di-2-nitro-*p*-tolyl diselenide.

Gentle warming with nitric acid gave (A), m. p. and mixed m. p. 151°. On treatment with equal volumes of nitric acid (*d* 1·41) and glacial acetic acid, the selenocyanate was unchanged, even after gentle warming.

Nitration unaccompanied by oxidation was effected by slowly adding the selenocyanate (3 g.) to nitric acid (*d* 1·5; 10 c.c.) at −10°. The solution was poured on ice (80 g.), and the precipitate (3·4 g.) crystallised from light petroleum, giving yellow needles (C), m. p. 69—70°, not depressing the m. p. of 2-*nitro*-p-*tolyl selenocyanate* obtained by the diazo-reaction; but in admixture with (B) obtained in the previous experiment, (C) melted at 54—55° (Found : N, 11·8. $C_8H_6O_2N_2Se$ requires N, 11·6%). The petroleum mother-liquors yielded relatively small amounts of a more soluble product (D) as yellow needles, m. p. 150°, not depressing the m. p. of 3-*nitro*-p-*tolyl selenocyanate* prepared in a yield of 70% from 3-nitro-*p*-toluidine (see p. 1374) (Found : Se, 32·45. $C_8H_6O_2N_2Se$ requires Se, 32·7%). The similarity in m. p. exhibited by the entirely dissimilar pairs of compounds (A) and (D) and (B) and (C) is of interest. A mixture of nitric acid (*d* 1·41) and sulphuric acid at −10° to −15° gave similar results, a certain amount of a nitrotolueneseleninic acid being also formed. The syntheses of (C) and (D) by means of the diazo-reaction are recorded in the table on p. 1374 [Found : (for C) N, 11·9; Se, 32·5; for (D) N, 11·9. $C_8H_6O_2N_2Se$ requires N, 11·6; Se, 32·7%].

Nitration of p-*Chlorophenyl Selenocyanate*.—The selenocyanate (11·5 g.) was treated with nitric acid (*d* 1·41; 42 c.c.) and sulphuric acid (42 c.c.) below 3°. After 2 hours, ice precipitated a yellow solid (14 g.), which was separated by alcohol into orange crystals (E; the main product), m. p. 89°, and a white solid (F), m. p. 180°. The m. p. of di-*p*-chlorophenyl diselenide (m. p. 89°), prepared from *p*-chlorophenyl selenocyanate and aqueous potassium hydroxide (Taboury, *Bull. Soc. chim.*, 1905, **35**, 673; Challenger, Peters, and Halévy, J., 1926, 1655), was not depressed on admixture with (E); and (F) was shown to be *p*-chlorobenzeneseleninic acid (Morgan and Elliott, P., 1914, **30**, 248), being soluble with effervescence in sodium bicarbonate solution and on reduction with zinc and hydrochloric acid giving the diselenide (E) (Found : Se, 35·4. Calc. for $C_6H_5O_2ClSe$: Se, 35·4%).

Similar results were obtained with sodium nitrate and sulphuric acid. Nitric acid (*d* 1·41) between −10° and 60° had no action on *p*-chlorophenyl selenocyanate. The action of equal volumes of acetic anhydride and nitric acid (*d* 1·5) at −10° gave the seleninic acid (F) and no trace of a nitro-compound.

Successful nitration was effected by treating the selenocyanate

(8 g.) with nitric acid (*d* 1·5; 25 c.c.) at −10°. Addition of ice after 1 hour gave a white solid (10 g.) which, when crystallised from alcohol, gave *p*-chlorobenzeneseleninic acid, m. p. 180°, and a small amount of pale yellow crystals (G), m. p. 127°, not depressing the m. p. of *2-nitro-*p*-chlorophenyl selenocyanate* prepared by the diazo-reaction (p. 1374) (Found for this synthetic specimen: N, 10·8; Se, 29·9. $C_7H_3O_2N_2ClSe$ requires N, 10·7; Se, 30·3%). The same result was obtained at −25°, 0°, 15° and 50°. At the last two temperatures, only traces of the nitro-selenocyanate were obtained, recognisable by the purple colour produced with alcoholic alkali.

Nitric Acid and p-*Bromophenyl Selenocyanate.*—Nitric acid (*d* 1·5; 20 c.c.) and the selenocyanate (7 g.) were allowed to react at −10°, and ice (50 g.) was added after 1 hour. The almost white solid (9 g.) obtained gave no colour with alcoholic alkali, had m. p. 177°, was wholly soluble in sodium bicarbonate solution, and after crystallisation from alcohol melted at 186° (decomp.). It was shown to be *p*-bromobenzeneseleninic acid (Found: Se, 29·0. Calc.: Se, 29·3%). Nothing further was isolated. Reduction of the seleninic acid with zinc and hydrochloric acid gave di-*p*-bromophenyl diselenide, m. p. 113°, not depressing the m. p. of the product obtained from *p*-bromophenyl selenocyanate and potassium hydroxide (Found: C, 31·0; H, 2·0; Se, 33·4. Calc. for $C_{12}H_8Br_2Se_2$: C, 30·7; H, 1·7; Se, 33·6%). The diselenide gives the seleninic acid on treatment with warm nitric acid (*d* 1·41). Taboury (*loc. cit.*) gives the m. p. of di-*p*-bromophenyl diselenide as 107°. It was, however, obtained from a very complex mixture and was probably slightly impure.

Preparation and Nitration of p-*Dithiocyanobenzene.*—(*a*) Preparative details are given on p. 1374. After treatment with charcoal and crystallisation from acetone–light petroleum, the dithiocyanate forms white needles, m. p. 106°, only slightly volatile with steam (Found: N, 14·8; S, 33·5. $C_8H_4N_2S_2$ requires N, 14·7; S, 33·3%). On treatment with 50% alcoholic potassium hydroxide, followed by acidification, the dimercaptan is obtained. This melts at about 95° and in air or on treatment with alcoholic ammonia gives a white, odourless, insoluble solid, decomp. about 330°, which is probably polymerised *p*-phenylene disulphide (Leuchart, *J. pr. Chem.*, 1890, **41**, 205).

(*b*) The dithiocyanate (5 g.) was treated with nitric acid (*d* 1·41; 7 c.c.) and sulphuric acid (7 c.c.) at 5°. Ice (20 g.), added after 2 hours, gave a precipitate (6 g.; m. p. 141°) which on crystallisation from alcohol formed yellow needles, m. p. 143—144° (Found: N, 17·7; S, 27·5. $C_8H_3O_2N_3S_2$ requires N, 17·7; S, 27·0%). The nitro-dithiocyanate did not depress the m. p. (143—144°) of the product obtained from 4-chloro(or bromo)-3-nitroaniline or from 2-nitro-4-thiocyanoaniline (see pp. 1373, 1374) by the diazo-reaction.

Preparation and Nitration of p-*Thiocyanoselenocyanobenzene.*—Preparative details are given on p. 1374. The crude reaction product was dried, extracted with chloroform, decolorised with charcoal, and crystallised from chloroform–light petroleum or from alcohol, giving white needles, m. p. 109—110°, which were somewhat volatile with steam and very soluble in acetone and chloroform (Found: N, 11·7; S, 13·8; Se, 32·9. $C_8H_4N_2SSe$ requires N, 11·7; S, 13·4; Se, 33·05%).

p-Thiocyanoselenocyanobenzene (2 g.) was dissolved in nitric acid (*d* 1·41; 6 c.c.) and sulphuric acid (7 c.c.) at 3°. Treatment with ice after 1 hour gave white crystals (1·5 g.), m. p. 154° after recrystallisation from acetone and alcohol. These contained sulphur, selenium, and nitrogen, were completely soluble in cold sodium bicarbonate solution or in hot water, gave no colour with alcoholic alkali, and contained either an SCN or an SeCN group as shown by the production of potassium thiocyanate on their reacting with alcoholic potassium hydroxide ($R{\cdot}SCN + KSH = RSK + HSCN$. $R{\cdot}SeCN + KSH = RSeK + HSCN$). The SeCN group had apparently been oxidised as before, giving *p*-thiocyanobenzeneseleninic acid (Found: N, 5·8; Se, 32·0. $C_7H_5O_2NSSe$ requires N, 5·7; Se, 32·1%). The use of nitric acid (*d* 1·41) or of the 95% acid alone or mixed with acetic acid or acetic anhydride at temperatures from −20° to 60° gave either the unchanged substance or the seleninic acid.

Nitro-derivatives of p-*Thiocyanoaniline and of* p-*Thiocyanoacetanilide.*—*p*-Thiocyanoaniline (Kaufmann and Oehring, *Ber.*, 1926, **59**, 189) was warmed with acetic anhydride, giving the acetyl derivative, m. p. 187° (Fichter and Beck, *Ber.*, 1911, **44**, 3636, give 181°). This (7·2 g.) was nitrated in a mixture of nitric acid (*d* 1·41; 17 g.) and sulphuric acid (25 g.) at 3°. Addition of ice after 2 hours gave a solid (9 g.), which crystallised from alcohol in yellow needles of 2-*nitro*-4-*thiocyanoacetanilide*, m. p. 138—139° (Found: N, 18·0; S, 13·7. $C_9H_7O_3N_3S$ requires N, 17·7; S, 13·5%). The mother-liquors yielded a small quantity of orange crystals, m. p. 113°, not depressing the m. p. of 2-*nitro*-4-*thiocyanoaniline* obtained by gently warming the nitro-acetanilide with hydrochloric acid for 10 minutes on the steam-bath. Dilution with ice gave a product, m. p. 113°, which was crystallised from aqueous alcohol (Found: N, 21·6; S, 16·3. $C_7H_5O_2N_3S$ requires N, 21·5; S, 16·4%). The prolonged action of hydrochloric acid on this substance gives red needles, m. p. 169°, which are possibly di-3-nitro-4-aminophenyl disulphide, but they have been only superficially examined

(Found: N, 16·15. Calc. for $C_{12}H_{10}O_4N_4S_2$; N, 16·5%). They are also obtained from 2-nitro-4-thiocyanoaniline and alcoholic alkali; the substance separates from acetone as yellow needles, which lose acetone at 100°, giving the red compound, m. p. 169°.

The position of the nitro-group in 2-nitro-4-thiocyanoaniline was determined by diazotisation in alcoholic solution, which gave rise to *m*-nitrophenyl thiocyanate, m. p. and mixed m. p. 56°. The diazo-group was also replaced by chlorine, bromine, thiocyanogen and selenocyanogen, giving (*a*) 4-*chloro*-3-*nitrophenyl thiocyanate*, m. p. 63°, not depressing the m. p. of the product obtained from 4-chloro-3-nitroaniline by the Sandmeyer reaction, (*b*) 4-*bromo*-3-*nitrophenyl thiocyanate*, m. p. 83°, pale yellow needles from light petroleum (Found: N, 11·0. $C_7H_3O_2N_2BrS$ requires N, 10·8%), (*c*) nitro-*p*-dithiocyanobenzene, m. p. 143—144° (see pp. 1365, 1371, and below), and (*d*) 2-*nitro*-4-*thiocyanophenyl selenocyanate*, m. p. 147°, yellow needles from alcohol, giving a purple colour with alcoholic alkali (Found: N, 14·9; Se, 27·3. $C_8H_3O_2N_3SSe$ requires N, 14·8; Se, 27·8%). In these preparations the nitrothiocyanoaniline was not isolated, the solution of its acetyl derivative in warm hydrochloric acid being diazotised (see table on p. 1374).

In the case of reactions summarised in this table further experimental details are omitted, the procedure closely resembling that employed in the preparation of such compounds as nitro-*o*-tolyl thiocyanate and phenyl selenocyanate (p. 1368); the yields are usually not less than 60—70%.

Abnormal Behaviour of 4-*Chloro* (and *bromo*)-3-*nitrobenzenediazonium Salts with Thiocyanates.*—4-Bromo-3-nitroaniline (22 g.) in dilute sulphuric acid (1 : 3) was diazotised at 3° with sodium nitrite (9 g.), and the solution slowly added in the cold to potassium thiocyanate (14·5 g.; 1·5 mols.) and cuprous thiocyanate (20 g.) in water. After 12 hours, the solid obtained was repeatedly extracted with alcohol. This finally yielded 9 g. of pale yellow needles (K), m. p. 143—144°, which were free from halogen, contained the thiocyano-group, and did not depress the m. p. of the product similarly obtained from 4-chloro-3-nitroaniline, or that of nitro-*p*-dithiocyanobenzene (p. 1371) obtained by nitration of *p*-dithiocyanobenzene or from 2-nitro-4-thiocyanoaniline (Found: N, 17·9; S, 27·5. Calc. for $C_8H_3O_2N_3S_2$: N, 17·7; S, 27·0%).

The alcoholic mother-liquors deposited a solid which, on repeated crystallisation from light petroleum, formed yellow needles (L; 10 g.), m. p. 83°, containing halogen and the thiocyano-group, and not depressing the m. p. of 4-bromo-3-nitrophenyl thiocyanate obtained from 2-nitro-4-thiocyanoaniline (above and p. 1374) (Found: N, 11·0. Calc. for $C_7H_3O_2N_2BrS$: N, 10·8%).

Base.	Wt. of base (g.).	H_2SO_4 (c.c.).	Acid : water.	Conc. HCl (c.c.).	$NaNO_2$ (g.).	KSCN (g.).	KSeCN (g.).	Cu' salt (g.).	Product.	M. p.	Coloration with alc. KOH.
$NH_2 : NO_2 : Cl = 1 : 3 : 4$	17	100	1 : 4	—	9·0	13·5	—	20·0	SCN : NO_2 : Cl = 1 : 3 : 4 SCN : NO_2 : SCN = 1 : 3 : 4	63° 144	Red „
$NH_2 : NO_2 : SCN = 1 : 2 : 4$	1·5 in 10 c.c. alcohol	10	conc.	—	0·5	—	—	—	H : NO_2 : SCN = 1 : 2 : 4	56	„
	3·0	—	—	10	0·9	—	—	2·5 in conc. HCl (30 c.c.)	Cl : NO_2 : SCN = 1 : 2 : 4	63	„
	8·0	—	—	30	3·6	—	—	12·0 in HBr (50 c.c.; *d* 1·49)	Br : NO_2 : SCN = 1 : 2 : 4		„
	3·0	—	—	10	2·0	1·7	—	4·0	SCN : NO_2 : SCN = 1 : 2 : 4	144	„
	12·0	—	—	35	4·5	—	11·0	—	SeCN : NO_2 : SCN = 1 : 2 : 4	147	Purple
NH_2 : SCN = 1 : 4	7·8	30	1 : 4	—	3·6	6·2	—	10·0	SCN : SCN = 1 : 4	106	—
	20·0	120	1 : 4	—	12·0	—	30·8	—	SeCN : SCN = 1	109·5	—
$NH_2 : NO_2 = 1 : 3$	14·0	50	1 : 3	—	9·0	—	21·0	—	SeCN : NO_2 = 1 : 3	65	Red
$NH_2 : NO_2 : CH_3 = 1 : 3 : 4$ $NH_2 : NO_2 : CH_3 = 1 : 2 : 4$	5·0	30	1 : 4	—	4·0	—	8·0	—	SeCN : NO_2 : CH_3 = 1 : 3 : 4 SeCN : NO_2 : CH_3 = 1 : 2 : 4	69·5 150	„ Purple
$NH_2 : NO_2 : Cl = 1 : 2 : 4$	5·0	25	1 : 3	—	2·5	—	7·0	—	SeCN : NO_2 : Cl = 1 : 2 : 4	127	„
NH_2 : NHAc = 1 : 4	7·5	40	1 : 3	—	4·5	—	11·0	—	SeCN : NHAc = 1 : 4	205	—

Analogous treatment of 4-chloro-3-nitroaniline (17 g.) gave (K), 9 g., m. p. 143—144°, and pale yellow needles (M; 10 g.), m. p. 63°, containing halogen and the thiocyano-group, not depressing the m. p. of 4-chloro-3-nitrophenyl thiocyanate obtained from 2-nitro-4-thiocyanoaniline (Found: N, 13·3. Calc. for $C_7H_3O_2N_2ClS$: N, 13·1%). When ferric thiocyanate was employed instead of the copper salt (Korczyński, *Bull. Soc. chim.*, 1922, **31**, 1179), the same products were obtained (K, 12·5 g.; M, 8 g.).

Nitro-derivatives of p-*Selenocyanoaniline and* p-*Selenocyanoacetanilide.*—*p*-Selenocyanoaniline (J., 1926, 1654) was dissolved in warm acetic anhydride, giving the *acetyl* derivative as white crystals, m. p. 206° (Found: N, 11·9. $C_9H_8ON_2Se$ requires N, 11·7%). This did not depress the m. p. of the product obtained from diazotised *p*-aminoacetanilide and potassium selenocyanate (see p. 1374), the reaction mixture being left for 1 day.

The selenocyanoacetanilide (4 g.) was added to nitric acid (*d* 1·5; 10 c.c.) at −20°, and the solution poured on ice after 1 hour. Fractional crystallisation of the yellow product gave almost equal amounts of yellow needles (H), m. p. 157°, and an almost white solid (J), m. p. 215°. (H) was found to be 2-*nitro*-4-*selenocyanoacetanilide* (Found: N, 15·2. $C_9H_7O_3N_3Se$ requires N, 15·0%). (J) was almost completely soluble in sodium bicarbonate solution and appeared to be a slightly impure seleninic acid. It has not been further examined.

On warming with hydrochloric acid, (H) gave a clear solution, from which ice precipitated a solid, forming, on crystallisation from aqueous alcohol, orange needles, m. p. 118°, which were 2-*nitro*-4-*selenocyanoaniline* (Found: N, 17·3. $C_7H_5O_2N_3Se$ requires N, 17·3%).

The selenium determinations were carried out by heating the substance with fuming nitric acid for 60 hours at 300°, evaporating the mixture with hydrochloric acid, and precipitating the selenium with sulphur dioxide. This method gives somewhat low results owing to volatilisation of selenium (Lyons and Shinn, *J. Amer. Chem. Soc.*, 1902, **24**, 1085; Bradt and Lyons, *ibid.*, 1926, **48**, 2642), but the error is not serious.

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