CCXV.—*The Introduction of the Selenocyano-group into Aromatic Compounds.*

By FREDERICK CHALLENGER, ARNOLD THORNTON PETERS, and JACOB HALÉVY.

IT was shown by Söderback (*Annalen*, 1919, **419**, 217; 1925, **443**, 142), by Kaufmann and Liepe (for references to several publications by Kaufmann, see *Ber.*, 1926, **59**, 178, 189), and by Challenger and Bott (J., 1925, **127**, 1039) that thiocyanogen reacts with amines and phenols, giving thiocyano-substitution products, and with unsaturated compounds to yield dithiocyano-additive compounds and sometimes monosubstitution products. One of us has also obtained additive compounds of thiocyanogen and triphenylarsine and triphenylstibine by two different methods (J., 1922, **121**, 101; 1923, **123**, 1048), but was unable to prepare triphenylbismuthine dithiocyanate, $BiPh_3(SCN)_2$, since this lost phenyl thiocyanate at the ordinary temperature. The close analogy existing between iodine and the thiocyanogen radical is well illustrated by these relations, since di-iodides of tertiary arsines and stibines, $(C_6H_5)_3MI_2$, are stable at the ordinary temperature, whilst triphenylbismuthine di-iodide loses iodobenzene below 0°, and other tertiary bismuthines behave similarly.

In July, 1924, one of the authors attempted the isolation of selenocyanogen, $(SeCN)_2$, in order to compare its properties with those of its sulphur analogue. The interaction of lead selenocyanate and bromine led to the formation of cyanogen triselenide, $(CN)_2Se_3$, at 0°, whilst at lower temperatures reaction was slow. It seemed probable, however, that cyanogen triselenide would undergo many of the reactions which might be expected in the case of selenocyanogen. This was found to be the case, but while the research was in progress Birckenbach and Kellermann (*Ber.*, 1925, **58**, 786, 2377) announced the isolation of selenocyanogen from silver selenocyanate and iodine, without, however, investigating it closely.

Quite recently, Kaufmann and Kögler (*Ber.*, 1926, **59**, 178) have shown that a mixture of lead tetra-acetate and potassium selenocyanate can be used as a source of nascent selenocyanogen. These authors also state that selenocyanogen reacts with aniline and α-naphthol, but give no details. In view of our analogous experiments with cyanogen triselenide, it was decided to publish the results so far obtained.

Triphenylbismuthine and the triselenide * react immediately in

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* Prepared by Verneuil's method (*Ann. Chim. Phys.*, 1886, **9**, 328). Selenium dicyanide also gives phenyl selenocyanate with the bismuthine.

ether, giving selenium, *phenyl selenocyanate* (see p. 1652), and diphenylselenocyanobismuthine, $BiPh_2·SeCN$. This unstable compound was identified by conversion into the corresponding iodo-derivative.

$$BiPh_3 + Se(SeCN)_2 = BiPh_2·SeCN + PhSeCN + Se.$$

From diphenylbromobismuthine and potassium selenocyanate, triphenylbismuthine and (apparently) decomposition products of bismuth selenocyanate were obtained, but no diphenylselenocyanobismuthine. An analogous decomposition is also observed with the more stable diphenylcyano- and diphenylthiocyano-bismuthines (J., 1922, **121**, 92).

Triphenylbismuthine dichloride and potassium selenocyanate at the ordinary temperature give phenyl selenocyanate: $BiPh_3Cl_2 + 2KSeCN = BiPh_2·SeCN + PhSeCN + 2KCl$. The diphenylselenocyanobismuthine was not isolated owing to its instability. The triphenylbismuthine which was also obtained may have arisen from its decomposition (see above), or thus: $BiPh_3Cl_2 + 2KSeCN = BiPh_3 + 2KCl + (SeCN)_2$. Tri-*p*-tolylbismuthine dichloride behaves analogously.

The selenocyano-radical, therefore, as was to be expected, resembles thiocyanogen and the relatively electropositive iodine rather than bromine, chlorine, or fluorine, which form bismuthine dihalides stable at the ordinary temperature.

The behaviour of triphenylstibine dichloride is noteworthy, *triphenylstibine hydroxyselenocyanate*, $SbPh_3(OH)·SeCN$, or possibly the corresponding *oxide*, $(SbPh_3·SeCN)_2O$, being readily isolated. This presumably arises from the action of traces of moisture on the unknown diselenocyanate. The same product is obtained from the stibine and cyanogen triselenide. No phenyl selenocyanate is formed in either case. The corresponding thiocyanates were similarly prepared from triphenylarsine and triphenylstibine or its dichloride (J., 1923, **123**, 1048).

We have supplemented these results by examining the behaviour of the tellurocyano-group. On grounds of analogy, triphenylbismuthine ditellurocyanide, $BiPh_3(TeCN)_2$, should be incapable of existence at the ordinary temperature, especially as no tellurocyanide, whether inorganic or organic, has yet been isolated. Since the preparation of tellurocyanogen, $(TeCN)_2$, might be expected to present considerable difficulties, tellurium dicyanide was chosen for interaction with triphenylbismuthine. Analogous experiments with sulphur dicyanide (J., 1922, **121**, 93) and selenium dicyanide (see p. 1648) gave rise to phenyl thiocyanate and selenocyanate, thus resembling the behaviour of thiocyanogen and cyanogen triselenide. The use of tellurium dicyanide therefore appeared to be admissible. It was prepared by the method of Cocksedge (J., 1908, **93**, 2175). With triphenylbismuthine in ether at the ordinary temperature, diphenylcyanobismuthine was obtained, and a red solid, m. p. 54°. This appeared to be diphenyl ditelluride (Lederer, *Ber.*, 1915, **48**, 1346), presumably a decomposition product of the phenyl tellurocyanide first formed :

$$BiPh_3 + CN{\cdot}TeCN = BiPh_2{\cdot}CN + PhTeCN.$$
$$2PhTeCN + 2H_2O = 2TeHPh + 2CNOH.$$
$$2TeHPh + O = Ph{\cdot}Te{\cdot}Te{\cdot}Ph + H_2O.$$

The thiocyanates and selenocyanates undergo a similar reaction in presence of air and alkali. Owing to the unstable nature of tellurium dicyanide and the poor yield obtained, this reaction has been effected only on a very small scale, but the anticipation that tellurocyanogen would be at least as electropositive as iodine appears to be justified.

Birckenbach and Kellermann (*loc. cit.*) have shown, by measurement of the decomposition potentials of the corresponding potassium salts in aqueous solution, that the halogens and pseudohalogens (a term introduced by these authors) may be arranged in the order F, ONC, OCN, Cl, N_3, Br, CN, SCN, I, SeCN, TeCN. The order of the elements F, Cl, Br, I is that of the stability of the tertiary bismuthine dihalides (J., 1915, **107**, 18; 1922, **121**, 91). The exact relative positions of CN, SCN, I, and SeCN are not so easily deduced from a study of their behaviour with tertiary bismuthines, but it is clear from the results so far described that they are all relatively electropositive. The results of some further experiments appear to favour the exact order given by Birckenbach and Kellermann, but these are reserved for a later communication. The decomposition of phenyl tellurocyanide and of tellurium cyanide in moist air at the ordinary temperature is in agreement with the position of the TeCN radical at the end of the table.

The relative positions of cyanogen and the halogens are also those required by the course of the reactions between cyanogen halides and triphenylbismuthine. With cyanogen iodide, iodobenzene is obtained, whereas benzonitrile is eliminated in the case of the bromide and chloride, a diphenylhalogenobismuthine being formed in each case. Wilkinson and Challenger (J., 1924, **125**, 855), in describing these results, stated "since in all analogous reactions the least negative radical is eliminated in union with the phenyl group (J., 1915, **107**, 17), it would appear that, as regards their negative properties, the radicals in question should be arranged in the order Cl > Br > CN > I."

A further analogy between cyanogen triselenide and thiocyanogen is afforded by its behaviour with aromatic bases. Aniline and cyanogen triselenide give p-*aminophenyl selenocyanate :*

$$C_6H_5{\cdot}NH_2 + Se_3(CN)_2 = C_6H_4(SeCN){\cdot}NH_2 + HSeCN + Se.$$
$$HSeCN = Se + HCN.$$

There was no trace of aniline selenocyanate or any similar compound, although in the analogous reaction with thiocyanogen aniline thiocyanate is produced. This is doubtless due to the instability of selenocyanic acid. Since Claus and Merck (*Ber.*, 1883, **16**, 2737) have shown that aromatic bases have scarcely any tendency to combine with hydrocyanic acid, the absence of aniline hydrocyanide is not surprising. The para-position of the selenocyano-group was proved by conversion into p-*chlorophenyl selenocyanate.*

The behaviour of dimethylaniline is analogous, selenium and p-*dimethylaminophenyl selenocyanate* being produced.

Dr. H. Phillips and Mr. F. C. Ray, to whom we communicated these results, have prepared large quantities of this substance and have converted it into p-*dimethylaminophenyl methyl selenide,*

$$Me_2N{\cdot}C_6H_4{\cdot}SeMe.$$

With acidified hydrogen peroxide, this loses selenium, yielding tetramethylbenzidine, thus establishing the para-position of the original selenocyano-group.

For the purposes of another research we have prepared phenyl selenocyanate (see J., 1924, **125**, 1380) and the corresponding p-*tolyl* and p-*bromophenyl* derivatives by the diazo-reaction. The nitration of these compounds is under investigation.

EXPERIMENTAL.

Triphenylbismuthine Dichloride and Potassium Selenocyanate.—The dichloride (3·55 g.; 1 mol.) and the selenocyanate (2 g.; 2 mols.) were shaken for 15 hours with 50 c.c. of dry light petroleum. The yellow solution was then decanted from the reddish-brown solid (A), replaced by more solvent, and shaking continued for a further 20 hours. The united petroleum extracts gave a yellow, oily solid (B), partly volatile in steam. The distillate yielded 0·9 g. of an oil with a strong odour of phenyl selenocyanate. This (0·5 g.), on nitration with 0·8 c.c. of nitric acid (*d* 1·41) and 0·8 c.c. of sulphuric acid at 0°, gave a pale yellow solid which, after being washed with water and thrice recrystallised from alcohol, had m. p. 141°, alone or mixed with *p*-nitrophenyl selenocyanate made from (*a*) phenyl selenocyanate by direct nitration, and (*b*) *p*-nitroaniline by the diazo-reaction. With alcoholic potash, it gave the red colour mentioned by Bauer (*Ber.*, 1913, **46**, 95), who gives, however, m. p. 135°. The presence of phenyl selenocyanate was confirmed by conversion into diphenyl diselenide (m. p. and mixed m. p. 65°).

The non-volatile portion of B was triphenylbismuthine, m. p. 79°. The solid (A) was extracted with hot benzene, leaving a residue (C). Light petroleum precipitated from the extract a solid which probably contained some diphenylselenocyanobismuthine (from analogy with the experiment described below). The solution yielded more bismuthine. Solid (C) still contained bismuth and selenium after treatment with water.

*Tri-*p*-tolylbismuthine Dichloride and Potassium Selenocyanate.*—The procedure was as in the previous experiment [dichloride, 5·1 g.; selenocyanate, 2·65 g.; light petroleum, (*a*) 40 c.c., (*b*) 30 c.c.; time of shaking, (*a*) 12 hours, (*b*) 4 hours]. From the petroleum on evaporation and steam distillation *p*-tolyl selenocyanate (see p. 1654), m. p. and mixed m. p. 55—56°, was obtained; it was characterised as the diselenide, m. p. and mixed m. p. 47·5°. The non-volatile portion, crystallised from alcohol, gave tri-*p*-tolylbismuthine, m. p. and mixed m. p. 119—120°, and a trace of di-*p*-tolyl diselenide. Di-*p*-tolylselenocyanobismuthine was doubtless produced in this reaction, but was not isolated owing to its instability.

Triphenylbismuthine and Cyanogen Triselenide.—The bismuthine (3·8 g.; 1 mol.) and the triselenide (2·5 g.; 1 mol.) were shaken in dry chloroform (30 c.c.) for 30 hours and the solid was then extracted with hot chloroform, leaving a residue (A, 1·35 g.). The united extracts on treatment with light petroleum gave a solid (B); the filtrate on concentration gave red selenium, and an oil which was partly volatile in steam, yielding phenyl selenocyanate. This was characterised as the diselenide, m. p. 65°. The non-volatile portion contained bismuthine and diselenide.

The solid (B) contained diphenylselenocyanobismuthine. With potassium iodide in dry ether, it gave a red solid and a yellow solution. The former contained potassium selenocyanate and phenyldi-iodobismuthine, whilst the solution yielded a yellow solid, m. p. 131°, containing iodine and tervalent bismuth (diphenyliodobismuthine melts at 132°: Gillmeister, *Ber.*, 1897, **30**, 2843). The residue (A) contained free selenium, and with hot hydrochloric acid gave benzene and red selenium, doubtless arising from a phenylselenocyanobismuthine.

Diphenylbromobismuthine and Potassium Selenocyanate.—Equal molecular quantities of these substances were shaken for 16 hours with dry benzene. A red solid formed almost immediately, but there was no odour of phenyl selenocyanate at any time. The solid was extracted with fresh benzene and finally with hot chloroform. All the extracts yielded triphenylbismuthine, whilst the insoluble, dark-brown solid resembled the product obtained from bismuth bromide and potassium selenocyanate. No diphenylselenocyanobismuthine could be detected.

Triphenylstibine Dichloride and Potassium Selenocyanate.—The dichloride (4·24 g.; 1 mol.) and the selenocyanate (2·88 g.; 2 mols.) were shaken in dry light petroleum for 4 days. The resulting solid (6·5 g.), on extraction with benzene, left a residue (A). The extract, on treatment with light petroleum, gave only colourless needles, m. p. 178°, which were halogen-free; no phenyl selenocyanate was produced.

For the estimation of selenium, the product was boiled for 30 minutes with hydrochloric acid, and the precipitated selenium extracted with chloroform to remove stibine derivatives. The acid filtrate gave no more selenium on treatment with sulphur dioxide. The selenium was redissolved in nitric acid, the solution evaporated with hydrochloric acid, treated with sulphur dioxide, and the selenium weighed (Found: Se, 16·2. $C_{19}H_{16}ONSbSe$ requires Se, 16·6%. $C_{20}H_{15}N_2SbSe_2$ requires Se, 28·1%). The product is therefore *triphenylstibine hydroxyselenocyanate*, or possibly the corresponding *oxide*, and not the diselenocyanate. On heating it, phenyl selenocyanate was produced. Hydrochloric acid gave triphenylstibine dichloride, which was isolated from the chloroform extract during the selenium estimation (m. p. and mixed m. p. 141°).

The original residue (A), after being washed with water and extracted with chloroform, was black and contained 91% of selenium.

Triphenylstibine and Cyanogen Triselenide.—The stibine (1·6 g.) and the triselenide (1·4 g.) were frequently shaken in cold, dry benzene during 6 hours. Red selenium and a white solid were quickly deposited. Selenium (0·68 g.; calc. for 2 atomic proportions, 0·70 g.) and 1·8 g. of triphenylstibine hydroxyselenocyanate were isolated in the usual manner. No trace of phenyl selenocyanate was detected.

Aniline and Cyanogen Triselenide.—Aniline (1 g.; 1 mol.) and the triselenide (3 g.; 1 mol.) were shaken with dry ether (40 c.c.) for 20 hours. A red solid (1·3 g.) and a deep yellow solution formed immediately. The solid, after extraction with hot chloroform, contained 96% of selenium. The ether yielded pale yellow crystals, m. p. 87—88°, which, after six recrystallisations from benzene–light petroleum, melted at 93·5°. No other products were isolated. With two molecular proportions of aniline the same product, contaminated with much unchanged aniline, was obtained. The selenium corresponded to two atomic proportions (Found: Se, 39·5, 39·7. $C_7H_6N_2Se$ requires Se, 40·1%). No portion of the reaction mixture gave a red colour or precipitate with cold hydrochloric acid, indicating the absence of the selenocyanate of an organic base. *Selenocyanoaniline* gave red selenium on continued boiling with hydrochloric acid. Sodium nitrite (0·2 g.) was slowly added to the base (0·2 g.) in hydrochloric acid (4 c.c.). Cuprous chloride (from copper carbonate, 0·2 g.) in hydrochloric acid was then added. Steam removed colourless plates, m. p. 55° (from light petroleum), which did not depress the m. p. of *p*-chlorophenyl selenocyanate obtained from *p*-chloroaniline.

Replacement of the amino-group by bromine in a similar manner gave yellow crystals, m. p. 116° after crystallisation from light petroleum. These contained bromine and were doubtless di-*p*-bromophenyl selenide, m. p. 115·5°. Both mono- and di-selenides are occasionally produced in this type of diazo-reaction.

Dimethylaniline and Cyanogen Triselenide.—The base (0·3 g.) and the triselenide (0·7 g.; 1 mol.) were shaken with dry ether for 18 hours. The black deposit (0·24 g.) contained Se, 92% (calc. for 2 atomic proportions, 0·36 g.). The ether yielded a substance which crystallised from alcohol in pale straw-coloured crystals, m. p. 105° (yield 90%) (Found: Se, 34·9; N, 12·2.* $C_9H_{10}N_2Se$ requires Se, 35·2; N, 12·4%). *Selenocyanodimethylaniline* is very soluble in most organic solvents.

p-*Tolyl Selenocyanate.*—A solution of 20 g. of *p*-toluidine in 106 c.c. of sulphuric acid (1 : 5) was diazotised at 3° (12 g. of sodium nitrite), made neutral to Congo-paper by addition of sodium acetate, and thereafter slowly added to 37·2 g. of potassium selenocyanate in 220 c.c. of cold water. After 16 hours, the dark solid with some selenium was separated, dried, and extracted with light petroleum in presence of animal charcoal, yielding large, transparent crystals of characteristic odour, m. p. 55—56° (Found: Se, 40·0, 39·95. C_8H_7NSe requires Se, 40·4%).

p-*Tolyl selenocyanate* is readily soluble in most organic solvents and is easily volatile in steam.

The petroleum mother-liquor yielded white needles (from alcohol) containing selenium, m. p. 69·5—70·5°; these were identified as di-*p*-tolyl selenide by oxidation with nitric acid and by conversion by hydrochloric acid into di-*p*-tolyl selenide dichloride, m. p. 177·5—178·5° after crystallisation from chloroform–light petroleum (Zeisèr, *Ber.*, 1895, **28**, 1670).

On boiling *p*-tolyl selenocyanate with alcoholic sodium hydroxide the diselenide, m. p. 47°, was obtained. Taboury (*Bull. Soc.*

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* Nitrogen determination by Dr. H. Phillips.

chim., 1906, **35**, 673) obtained this substance from magnesium *p*-tolyl bromide and selenium.

p-*Bromophenyl Selenocyanate.*—The procedure for the preparation was as in the preceding experiment [*p*-bromoaniline, 15 g.; sulphuric acid (1 : 5), 85 c.c.; sodium nitrite, 7 g.; sodium acetate; potassium selenocyanate, 21 g. in 135 c.c. of water at 0°]. The solid product gave, on distillation with steam, a substance which crystallised from light petroleum in white needles, m. p. 70·5—71·5° (Found: Se, 30·1. C_7H_4NBrSe requires Se, 30·3%). The non-volatile portion yielded much di-*p*-bromophenyl diselenide, which was also obtained from the selenocyanate and alcoholic potassium hydroxide; it had m. p. 106—107° (Taboury, *loc. cit.*, gives m. p. 107°).

p-*Chlorophenyl Selenocyanate.*—This was prepared analogously to the bromo-derivative, and after treatment with charcoal in light petroleum, formed colourless needles, m. p. 53·5—54·5°. Morgan and Elliott (P., 1914, **30**, 248) obtained yellow leaflets from alcohol, m. p. 50—51°.

On boiling with alcoholic potassium hydroxide di-*p*-chlorophenyl diselenide, m. p. 85—87°, was obtained (compare Taboury, *loc. cit.*).

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