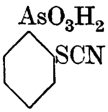
CCCLXII.—*Aromatic Arsenic Compounds containing Sulphur Groups attached to the Nucleus. Part II. Thiocyano- and Disulphido-groups.*

By Harry James Barber.

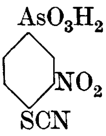
In Part I (this vol., p. 2047) the preparation of various sulphoarsinic acids was described; the present paper deals with bivalent sulphur substituents.

The methods involving the coupling of diazo-compounds with alkali sulphides, to form thiol or disulphide derivatives, are not suitable in the arsenical series on account of the formation of thioarsinites by interaction of the arsinic acid group and the sulphides. The application of the xanthate reaction to the preparation of sulphonic acids, with the disulphide as a by-product, has already been described (King, J., 1926, 1359).

The introduction of the thiocyano-group has now been found practicable in certain instances by the diazo-reaction and potassium cuprothiocyanate. 4-*Thiocyano*-, 2-*thiocyano*- (I), and 3-*nitro*-4-*thiocyano-phenylarsinic acids* (II) have been obtained in this way.



(I.)



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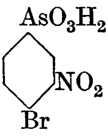

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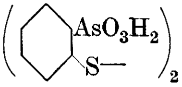


(IV.)

It is remarkable that 4-bromo-3-nitrophenylarsinic acid (III) does not yield the 3-nitro-4-thiocyano-acid with potassium thiocyanate, whereas 2 : 4-dinitrobromobenzene readily reacts to give the thiocyano-derivative.

2-Thiocyanophenylarsinic acid is comparatively unstable and readily decomposes into an amorphous substance which on mild oxidation gives *diphenyl disulphide* 2 : 2′-*diarsinic acid* (IV).

4-Thiocyanophenylarsinic acid on hydrolysis with sodium hydroxide passes by similar stages to the diphenyl disulphide 4 : 4′-diarsinic acid described by King (*loc. cit.*).

In a similar way the disulphides themselves are partly transformed into amorphous materials, insoluble in weak alkalis, which on mild oxidation regenerate the crystalline disulphide arsinic acids. This behaviour is attributed to the interaction of the thiol group, formed by hydrolysis of the thiocyano-group, $R{\cdot}SCN + 3NaOH = R{\cdot}SNa + Na_2CO_3 + NH_3$, or disulphido-group (Smiles, J., 1921, **119**, 1794), $R{\cdot}S{\cdot}S{\cdot}R + 2NaOH = R{\cdot}SNa + R{\cdot}SONa + H_2O$, with the arsinic acid group according to the general equation (Barber, J., 1929, 1020)

$$R{\cdot}AsO_3H_2 + 4R'SH = R{\cdot}As(SR')_2 + R'{\cdot}S{\cdot}S{\cdot}R' + 3H_2O,$$

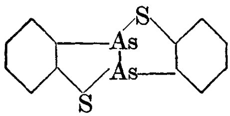
thus giving a complex intramolecular thioarsinite of the type $[{-}S{\cdot}C_6H_4{\cdot}As(S{\cdot}C_6H_4{\cdot}As{<})_2]_n$ which obviously on oxidation will regenerate the disulphide arsinic acid. In fact, any process calculated to give a thiol-arsinic acid appears to give products such as the above and it seems probable that an arsinic acid containing a free thiol group will at any rate be very unstable if the thiol group is at all reactive. Krishna and Krishna (*J. Indian Chem. Soc.*, 1929, **6**, 672) state that they have obtained 4-thiolphenylarsinic acid by oxidising the corresponding arseno-derivative for several hours at 100° with alkaline hydrogen peroxide. The thioarsinites and disulphides described here all pass readily under such conditions to the sulphonic acids. It is extremely unlikely that any thiol group could remain intact under such treatment; the disulphide at least would be formed. Moreover, the xanthate process by which Krishna and Krishna claim to have prepared 4 : 4′-dithiolarsenobenzene has already been shown by King (*loc. cit.*) to give *p*-xanthylphenylarsinic acid.

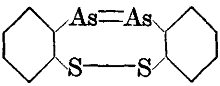
3-Nitro-4-thiocyanophenylarsinic acid on hydrolysis with alkali loses the sulphur group, as might be expected by analogy with 2 : 4-dinitrophenyl thiocyanate (Challenger and Collins, J., 1924, **125**, 1381). In the hydrolysis of this substance cold caustic alkali produces an intense bluish-violet colour which fades slowly, and the same colour is produced in mild alkalis by the action of hydrogen peroxide.

The nitration of 4-thiocyanophenylarsinic acid was attempted but was unsuccessful, since mild conditions gave no nitration (compare nitration of the corresponding halogen compounds; J., 1929, 233) and more vigorous conditions gave disulphide or sulphonic acid.

2-Sulphinophenylarsenious oxide (Part I, *loc. cit.*) gives on mild reduction, followed by oxidation of the arsinoxide to arsinic acid, the disulphide arsinic acid (IV). Stronger reducing agents yield an unusual substance to which is given the structure (V).

(V.)





(VI.)

It is also formed by reduction of 2-thiocyanophenylarsinic acid or the corresponding disulphide. The structure (V) is to be preferred to a normal arseno-structure (VI), since the compound possesses few of the normal properties of such substances. For instance, arseno-compounds are generally amorphous substances of high molecular weight, insoluble in organic solvents and have no definite melting points. The few simple arseno-compounds that have been obtained crystalline tend to polymerise and on formation they are usually accompanied by the polymeric forms (see, *e.g.*, Palmer and Scott, *J. Amer. Chem. Soc.*, 1928, **50**, 537; Bhede and Smith, *ibid.*, 1930, **52**, 2947). This substance (V) on the contrary is a unimolecular crystalline substance with no obvious tendency to polymerise and with a sharply defined melting point (177—178°). It is relatively stable towards oxidation, but can be converted into the disulphide arsinic acid (IV) and into 2-sulphophenylarsinic acid.

EXPERIMENTAL.

4-*Thiocyanophenylarsinic Acid.*—4-Aminophenylarsinic acid (11 g.), dissolved in *N*-hydrochloric acid (140 c.c.), was diazotised with sodium nitrite (3·5 g.) in water (20 c.c.), the solution added to a solution of cuprous thiocyanate (6 g.) in water (17 c.c.) containing potassium thiocyanate (35 g.), and the whole kept for some hours at room temperature. The mixture of cuprous thiocyanate and *arsinic acid* was then removed and extracted with sodium bicarbonate solution, which gave the required acid on acidification. The mother-liquor from the cuprous thiocyanate sometimes deposited a further crop of acid which only crystallised slowly. Attempts to concentrate the filtrate in order to obtain further crops resulted in the formation of tarry or amorphous matter. The yield was small (30%). The acid formed prisms from hot water or dilute acetic acid (Found: As, 28·5; N, 5·35. $C_7H_6O_3NSAs$ requires As, 28·95; N, 5·4%).

Diphenyl Disulphide 4 : 4′-*Diarsinic Acid.*—4-Thiocyanophenylarsinic acid (1 g.) was boiled with 2*N*-sodium hydroxide solution (10 c.c.) until evolution of ammonia ceased. The amorphous material which separated on acidification was collected, suspended in excess of sodium bicarbonate solution, and treated with a solution of iodine in potassium iodide until solution ensued. After filtration (charcoal) and acidification (hot) the required disulphide crystallised (Found: As, 31·8. Calc.: As, 32·2%). The disulphide can also be obtained directly from the liquor in the preparation of 4-thiocyanophenylarsinic acid by removal of cuprous thiocyanate on completion of the reaction, followed by addition of sodium hydroxide (30 g.) and hydrolysis as above. Yield, 4—5 g.

2-*Thiocyanophenylarsinic Acid* (I).—The reaction was carried out exactly as for the 4-isomeride (Found: As, 27·7. $C_7H_6O_3NSAs$

requires As, 28·95%). Attempts to recrystallise the crude product always resulted in the formation of the disulphide.

Diphenyl Disulphide 2 : 2′-*Diarsinic Acid* (IV).—(1) The crude 2-thiocyanophenylarsinic acid was hydrolysed wtih 2*N*-sodium hydroxide and treated as for the 4-isomeride (Found: As, 31·5; S, 14·1. $C_{12}H_{12}O_6S_2As_2$ requires As, 32·2; S, 13·75%).

(2) 2-Sulphinophenylarsenious oxide (2 g.), dissolved in alcohol (20 c.c.) saturated with sulphur dioxide and containing a trace of hydrogen iodide, was boiled for ¼ hour and the remaining sulphur dioxide was removed by aeration. The alcohol was removed and the residue oxidised in the usual way. The product was purified by acidification of a boiling solution in aqueous sodium bicarbonate (Found: As, 31·3, 31·4%).

(3) 2-Sulphinophenylarsenious oxide (2 g.) in water (200 c.c.) containing sulphuric acid (25 c.c. of 2*N*) and hydrogen iodide (2 drops, *d* 1·7) was heated for 2 days at 95°. The product was collected and oxidised as above (Found: As, 30·8; S, 14·2%).

It is evident that the disulphide was in each case contaminated with the disulphoxide, which is almost invariably formed in the conversion of a sulphinic acid into disulphide or in the hydrolysis of a disulphide by alkali. The disulphide as obtained by any of the above methods appeared to be homogeneous and formed small prisms on acidification of a hot, very dilute sodium bicarbonate solution. It was extremely sparingly soluble in water, glacial acetic acid, or alcohol.

The following experiment illustrates the hydrolysis by alkali. The disulphide (0·2 g.) was heated for ¼ hour at 95° in *N*-sodium hydroxide (10 c.c.), 2*N*-hydrochloric acid (6 c.c.) was added, and the resulting suspension of amorphous thioarsinite was titrated with *N*/10-iodine: the 4·5 c.c. required indicated 52% hydrolysis to thiol or thioarsinite. The disulphide does not absorb iodine in aqueous suspension.

3-*Nitro*-4-*thiocyanophenylarsinic Acid* (II).—3-Nitro-4-aminophenylarsinic acid (13 g.) was diazotised by solution in *N*/2-sodium hydroxide solution (50 c.c.) containing sodium nitrite (3·5 g.) and addition to a solution of hydrochloric acid (14 c.c.; *d* 1·16) in water (50 c.c.) at 20°. The diazo-solution was treated as for the 2- and 4-thiocyano-acids. The *arsinic acid* (yield, 50%) formed yellow leaflets from hot water (Found: As, 25·0; N, 9·4. $C_7H_5O_5N_2SAs$ requires As, 24·7; N, 9·2%).

After boiling with 2*N*-sodium hydroxide solution until evolution of ammonia ceased, the solution was acidified with dilute hydrochloric acid. Sulphur dioxide was liberated and a brown tarry material precipitated. This material did not yield 3-nitro-4-hydroxyphenylarsinic acid as anticipated.

Substance (V).—A solution of 2-sulphinophenylarsenious oxide (4·6 g.) in hot glacial acetic acid (40 c.c.) and hypophosphorous acid (20 c.c.; *d* 1·14) to which potassium iodide (3·2 g.) had been added was boiled for 5 minutes. A slight odour of thiophenol was noticed, suggesting elimination of arsenic. The crystalline *product* was washed with a little alkali to remove any unchanged sulphinic acid; yield, 3·5 g. (95%). It formed lemon-yellow prisms, m. p. 177—178°, from glacial acetic acid, benzene, or alcohol, in all of which it was somewhat difficultly soluble (Found: As, 40·9; S, 17·8; C, 39·3; H, 2·2; *M*, in camphor, 330, 380, 357. $C_{12}H_8S_2As_2$ requires As, 41·0; S, 17·5; C, 39·3; H, 2·2%; *M*, 366).

The same product was obtained on reduction of the sulphinic acid with sodium hyposulphite or zinc and hydrochloric acid or by reduction of the 2 : 2′-disulphide or 2-thiocyanophenylarsinic acid with sodium hyposulphite or hypophosphorous acid.

The substance was unaffected by boiling alkali but dissolved in concentrated sulphuric acid with a yellow-orange colour. It was slowly oxidised by iodine in bicarbonate suspension, giving the disulphide arsinic acid. Concentrated nitric acid rapidly oxidised it to 2-sulphophenylarsinic acid. Heating at about 300° produced a complex decomposition and no product of distillation could be identified. Similarly, heating with copper bronze (Naturkupfer C) did not yield thianthren as might be expected on simple removal of the arsenic.

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