CCXXII.—*The Reaction between Aminophenylarsinic Acids and Carbon Disulphide.*

By JOHN GARWOOD EVERETT.

THE reaction in which an aminophenylarsinic acid is boiled with alcohol and carbon disulphide in presence of excess of sodium hydroxide with formation of a thiocarbonylarylarsenic disulphide (or sesquisulphide) (J., 1929, 670) has now been studied in detail.

As far as the amine is concerned, there are two possibilities, namely, formation of a thiocarbimide RNCS or of a dithiourea RNH·CS·NHR. Ring closure occurs in the second instance in the case of *o*-diamines and *o*-aminophenols, giving respectively 2-thiolbenziminazoles and 1-thiobenzoxazolones. In each case one molecule of carbon disulphide causes the liberation of one molecule of hydrogen sulphide only, which is insufficient to account for the yield of thiocarbonylarylarsenic disulphide (or sesquisulphide) obtained (see Tables I and II; and Schulte, *Ber.*, 1882, **15**, 1955; Morgan, " Organic Compounds of Arsenic and Antimony," p. 75). Side reactions must therefore occur in which hydrogen sulphide is formed independently of any reaction involving the amino-group, and this has been proved by carrying out the reaction with phenylarsinic acid, phenylarsenic sesquisulphide being isolated from the product.

This independent formation of hydrogen sulphide is readily accounted for by alkaline hydrolysis of sodium ethyl xanthate or

TABLE I.

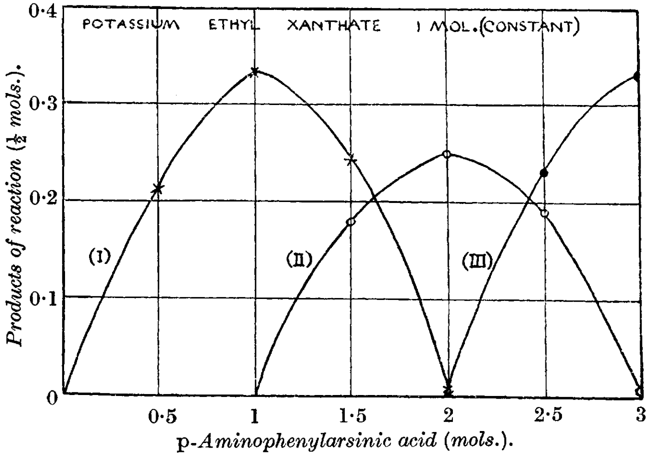
Substances reacting.				Products of reaction.							
Potassium ethyl xanthate.	Carbon disulphide.	Phenylarsinic acid.	*p*-Aminophenylarsinic acid.	Phenylarsenic sesquisulphide, $(C_6H_5{\cdot}As)_2S_3$.	Phenylarsinic acid (unchanged).	*pp'*-Dithiocarbiminophenylarsenic sesquisulphide, $(SCN{\cdot}C_6H_4{\cdot}As)_2S_3$ (I).	Diphenylthiourea-*pp'*-arsenic sesquisulphide, $CS(NH{\cdot}C_6H_4{\cdot}As)_2S_3$ (II).	Diphenylthiourea-*pp'*-diarsinic acid, $CS(NH{\cdot}C_6H_4{\cdot}AsO_3H_2)_2$ (III).	*p*-Aminophenylarsinic acid (unchanged).	Arsenious acid (represented as the equivalent number of grams of As_2S_3).	Arsenious sulphide.
	60 g., 8 mols.		22 g., 1 mol.			18 g. 0·7 half mol.				2 g.	
	60 g., 8 mols.	20 g., 1 mol.		2 g., 0·1 half mol.	6 g., 0·27 mol.					1 g.	3 g.
32 g., 2 mols.		20 g. 1 mol.		2 g.,* 0·1 half mol.	5 g., 0·25 mol.					1 g.	5 g.
16 g., 1 mol.			11 g., 0·5 mol.			5 g., 0·21 half mol.				1·5 g.	
16 g., 1 mol.			22 g., 1 mol.			8 g., 0·33 half mol.				3 g.	
16 g., 1 mol.			33 g., 1·5 mol.			6 g., 0·24 half mol.	4·3 g., 0·18 half mol.		5 g., 0·23 mol.	4 g.	
16 g., 1 mol.			44 g., 2 mols.			1 g., 0·04 half mol.	6 g., 0·25 half mol.	0·5 g., 0·03 half mol.	9 g., 0·41 mol.	5 g.	
16 g., 1 mol.			55 g., 2·5 mols.				4·4 g., 0·19 half mol.	5 g., 0·23 half mol.	14 g., 0·63 mol.	6 g.	
16 g., 1 mol.			66 g., 3 mols.				1 g., 0·04 half mol.	7 g., 0·33 half mol.	20 g., 0·91 mol.	7 g.	

* When two mols. of the original acid are involved in the formation of one mol. of product, the latter is given in half-mols.

sodium metathiocarbonate, the latter being formed by solution of carbon disulphide in sodium hydroxide solution. Some de-arsenication occurred in each case, the final liquors always containing arsenious acid. In the case of phenylarsinic acid, arsenic trisulphide was also formed.

The reaction was next studied with potassium ethyl xanthate in place of carbon disulphide. This allowed more variation, since carbon disulphide gave satisfactory results only when used in excess. The proportions of alcohol and sodium hydroxide solution were kept constant and the same as before, and the period of boiling under reflux was the same. The result obtained with two mols. of xanthate and one of phenylarsinic acid was almost identical with that obtained when excess of carbon disulphide was used (Table I).

FIG. 1.



The case of p-aminophenylarsinic acid is summarised in Table I and Fig. 1, which show the effect of increasing the amount of the acid in the initial reaction mixture, the amount of potassium ethyl xanthate remaining constant and equal to one mol.

The presence of an excess of potassium ethyl xanthate favours the formation of pp'-dithiocarbiminophenylarsenic sesquisulphide (I), the amount formed reaching a maximum when one mol. of p-aminophenylarsinic acid is present, and decreasing to zero with the presence of just over two mols. As the formation of (I) begins to decrease, diphenylthiourea-pp'-arsenic sesquisulphide (II) begins to appear in the final mixture, and the amount of this sulphide formed reaches a smaller maximum when two mols. of p-aminophenylarsinic acid are initially present, and falls to zero with the presence of about three mols. As the formation of the sulphide (II)

TABLE II.

Substances reacting.				Products of reaction.						
Potassium ethyl xanthate.	Carbon disulphide.	3-Amino-4-hydroxyphenylarsinic acid.	3 : 4-Diaminophenylarsinic acid.	1-Thiobenzoxazolone-4-arsenic disulphide,  (IV).	1-Thiobenzoxazolone-4-arsinic acid,  (V).	3-Amino-4-hydroxyphenylarsinic acid (unchanged).	2-Thiolbenziminazole-5-arsenic disulphide,  (VI).	2-Thiolbenziminazole-5-arsinic acid,  (VII).	3 : 4-Diaminophenylarsinic acid (unchanged).	Arsenious acid (represented as the equivalent number of grams of As_2S_3).
	60 g., 8 mols.	23·4 g., 1 mol.		18 g., 0·62 mol.						2·5 g.
	60 g., 8 mols.		23·4 g., 1 mol.				18 g., 0·62 mol.			2·5 g.
16 g., 1 mol.		11·7 g., 0·5 mol.		5·9 g., 0·24 mol.						1 g.
16 g., 1 mol.		23·4 g., 1 mol.		8 g., 0·33 mol.	4 g., 0·15 mol.	3 g., 0·13 mol.				2 g.
16 g., 1 mol.		35·1 g., 1·5 mols.		7·5 g., 0·31 mol.	11·2 g., 0·42 mol.	4 g., 0·17 mol.				3 g.
16 g., 1 mol.		46·8 g., 2 mols.		6 g., 0·25 mol.	16 g., 0·6 mol.	6 g., 0·26 mol.				5 g.
16 g., 1 mol.			11·7 g., 0·5 mol.				6 g., 0·25 mol.			1·2 g.
16 g., 1 mol.			23·3 g., 1 mol.				8·1 g., 0·33 mol.	3·9 g., 0·14 mol.	3 g., 0·13 mol.	2 g.
16 g., 1 mol.			35·1 g., 1·5 mols.				7·5 g., 0·31 mol.	11·0 g., 0·41 mol.	3·7 g., 0·16 mol.	3·3 g.
16 g., 1 mol.			46·6 g., 2 mols.				6 g., 0·25 mol.	15·5 g., 0·58 mol.	6 g., 0·26 mol.	4·5 g.

decreases, diphenylthiourea-*pp*′-diarsinic acid (III) makes its appearance, the amount formed increasing as the amount of *p*-aminophenylarsinic acid initially present is increased. In all cases some de-arsenication occurred.

These results show that in presence of excess of potassium ethyl xanthate, or even when molecular proportions of xanthate and *p*-aminophenylarsinic acid are taken, the reaction proceeds entirely according to the equation

$$\mathrm{R{\cdot}NH_2 + SC(OEt){\cdot}SK = R{\cdot}NCS + KSH + EtOH},$$

whereas in presence of more than one mol. excess of *p*-aminophenylarsinic acid the reaction proceeds entirely according to the equation

$$\mathrm{2R{\cdot}NH_2 + SC(OEt){\cdot}SK = (R{\cdot}NH)_2CS + KSH + EtOH.}$$

When the excess of *p*-aminophenylarsinic acid exceeds two mols. the proportion of potassium hydrosulphide in the reaction mixture becomes so small that the arsinic acid group is not attacked, hence diphenylthiourea-*pp*′-diarsinic acid (III) only is formed. That the thiocarbimide only is formed when carbon disulphide is used is due to the fact that in this case the reaction only proceeds satisfactorily in presence of a large excess of carbon disulphide.

These conclusions are borne out by the results obtained in the case of 3-amino-4-hydroxyphenylarsinic acid and 3 : 4-diaminophenylarsinic acid, which may be considered together, and are recorded in Table II. In both cases excess of potassium ethyl xanthate favours formation of the thiocarbonylarylarsenic disulphide, while excess of either arsinic acid decreases the amount of disulphide formed, an increased amount of either 1-thiobenzoxazolone-4-arsinic acid (V) or 2-thiolbenziminazole-5-arsinic acid (VII) being obtained. Some dearsenication occurs in both instances.

EXPERIMENTAL.

Phenylarsinic Acid and Carbon Disulphide.—Phenylarsinic acid (20 g.) and carbon disulphide (60 g.) were boiled under reflux with ethyl alcohol (200 c.c.) for 2 hours and cooled, sodium hydroxide solution (25%; 50 c.c.) was added, and boiling continued for 4 hours. Alcohol and carbon disulphide were then removed by distillation and the liquid residue was diluted and acidified (Congo-red) with hydrochloric acid, which precipitated a yellow sticky mass. The liquor was decanted and retained (A). The yellow mass was extracted several times with carbon disulphide; the residual yellow powder, after being washed with alcohol and dried at 80°, proved to be arsenious sulphide (3 g.) (Found : As, 60·8; S, 38·9%). The carbon disulphide extract was evaporated on a water-bath, leaving a pale yellow oil which, after repeated solution in cold benzene, followed by evaporation, crystallised in pale yellow prisms, and proved to be phenylarsenic sesquisulphide (2 g.), m. p. (alone or mixed with an authentic specimen) 130° (Found : As, 37·4; S, 24·1. Calc. : As, 37·5; S, 24·0%).

The liquor (A) was neutralised with sodium bicarbonate, evaporated nearly to dryness on a water-bath, and acidified (Congo-red) with hydrochloric acid, unchanged phenylarsinic acid crystallising (6 g.) (Found : As, 37·1. Calc. : As, 37·1%). The filtrate yielded arsenious sulphide (1 g.) when saturated with hydrogen sulphide.

Phenylarsinic Acid and Potassium Ethyl Xanthate.—The procedure was exactly as described above, carbon disulphide being replaced by potassium ethyl xanthate (32 g.). Phenylarsinic acid (20 g.) gave arsenious sulphide (5 g.), phenylarsenic sesquisulphide, m. p. 130° (2 g.), and unchanged phenylarsinic acid (5 g.). The final liquor gave arsenious sulphide (1 g.) when saturated with hydrogen sulphide.

p-*Aminophenylarsinic Acid and Carbon Disulphide.*—The procedure was that previously described (J., 1929, 670). *p*-Aminophenylarsinic acid (22 g.) gave *pp'*-dithiocarbiminophenylarsenic sesquisulphide (18 g.). The mother-liquor from the crude sulphide on saturation with hydrogen sulphide gave arsenious sulphide (2 g.).

3-*Amino*-4-*hydroxyphenylarsinic Acid and Carbon Disulphide.*—The acid (23·4 g.) gave 1-thiobenzoxazolone-4-arsenic disulphide (18 g.) and arsenious sulphide (2·5 g.).

3 : 4-*Diaminophenylarsinic Acid and Carbon Disulphide.*—The acid (23·4 g.) gave 2-thiolbenziminazole-5-arsenic disulphide (18 g.) and arsenious sulphide (2·5 g.).

p-*Aminophenylarsinic Acid and Potassium Ethyl Xanthate* (*Typical Examples*).—(*a*) *p*-Aminophenylarsinic acid (55 g.; 2·5 mols.) and potassium ethyl xanthate (16 g.; 1 mol.) were boiled under reflux with ethyl alcohol (500 c.c.) and water (50 c.c.) for 2 hours and cooled, sodium hydroxide solution (25%; 150 c.c.) was added, and boiling continued for 4 hours. Alcohol and carbon disulphide were then removed by distillation, the liquid residue was diluted with water while hot, cooled, and acidified (Congo-red) with hydrochloric acid, sufficient acid being added to keep any unchanged *p*-aminophenylarsinic acid in solution. The precipitate (A) was removed by filtration and washed with water, the combined filtrate and washings being retained (B). The precipitate (A) was suspended in water, and sodium bicarbonate added till no more effervescence occurred. The solution was then treated with charcoal and filtered, the residue being retained (C). The filtrate on acidification with hydrochloric acid yielded diphenylthiourea-

pp'-diarsinic acid, which was dissolved in sodium bicarbonate solution, treated with charcoal, and reprecipitated (yield, 5 g.) (Found for acid dried at 80° : As, 31·4; N, 5·8; S, 6·8. Calc.: As, 31·5; N, 5·9; S, 6·7%).

The residue (C) after drying was treated with carbon disulphide to remove sulphur, washed with alcohol, and dried at 60°. It proved to be diphenylthiourea-*pp'*-arsenic sesquisulphide (yield, 4·4 g.) (Found: As, 29·4; N, 5·4; S, 25·3; atomic ratios As : N : S = 1·00 : 0·98 : 2·02. Calc.: As, 31·8; N, 5·9; S, 27·1%). On reduction with sodium hyposulphite it gave *pp'*-arseno(diphenylthiourea), *insoluble* in sodium hydroxide solution (distinction from *pp'*-dithiocarbiminophenylarsenic sesquisulphide). The unchanged *p*-aminophenylarsinic acid was recovered from the combined filtrate and washings (B) by neutralising them with sodium hydroxide, concentrating the solution, and making it just acid (Congo-red) with hydrochloric acid; it was recrystallised by solution in dilute hydrochloric acid, filtration, and addition of sodium acetate solution (yield, 14 g.) (Found for acid dried at 80° : As, 34·5. Calc.: As, 34·6%). The filtrate from the crude arsanilic acid yielded arsenious sulphide (6 g.) when saturated with hydrogen sulphide.

(*b*) *p*-Aminophenylarsinic acid (33 g.; 1·5 mols.) and potassium ethyl xanthate (16 g.; 1 mol.) were boiled under reflux with ethyl alcohol (300 c.c.), water (30 c.c.), and sodium hydroxide solution (25%; 100 c.c.) as above described. Acidification of the diluted liquid residue after removal of alcohol and carbon disulphide yielded an amorphous powder (A), which was removed by filtration, the combined filtrate and washings being retained (B). The precipitate (A) was completely soluble in aqueous sodium hydroxide, the solution giving a deep violet colour with alkaline sodium nitroprusside. It was reduced with sodium hyposulphite solution (as described in J., 1929, 675) and the product was treated with cold sodium hydroxide solution (5%), the residue being retained (C). The solution so obtained, on acidification (Congo-red) with hydrochloric acid, yielded *pp'*-dithiocarbiminoarsenobenzene, which was washed with water and dried in a vacuum over concentrated sulphuric acid (Found: As, 34·4; N, 6·4; S, 14·8; atomic ratios As : N : S = 1·00 : 0·99 : 1·01. Calc.: As, 35·9; N, 6·7; S, 15·3%). Yield, 4·9 g., equivalent to 6 g. of *pp'*-dithiocarbiminophenylarsenic sesquisulphide (I).

The residue (C) was washed with water and dried in a vacuum over concentrated sulphuric acid. It was insoluble in sodium hydroxide solution and proved to be *pp'*-arseno(diphenylthiourea) (Found: As, 36·4; N, 6·8; S, 7·9; atomic ratios As : N : S = 2·00 : 2·00 : 1·02. Calc.: As, 39·9; N, 7·4; S, 8·5%). Yield, 3·4 g., equivalent to 4·3 g. of diphenylthiourea-*pp′*-arsenic sesquisulphide (II). *Note.* A direct separation of the sulphides (I) and (II) is not possible.

Unchanged *p*-aminophenylarsinic acid was recovered from the combined filtrate and washings (B) as described in (*a*) above (yield, 5 g.). The filtrate from the crude acid gave arsenious sulphide (4 g.) when saturated with hydrogen sulphide.

3-*Amino*-4-*hydroxyphenylarsenic Acid and Potassium Ethyl Xanthate* (*Typical Example*).—3-Amino-4-hydroxyphenylarsinic acid (46·8 g.; 2 mols.) and potassium ethyl xanthate (16 g.; 1 mol.). were boiled under reflux with ethyl alcohol (400 c.c.) and water (40 c.c.) for 2 hours and cooled, sodium hydroxide solution (25%; 120 c.c.) was added, and boiling continued for 4 hours. The subsequent treatment was exactly as described under (*a*) above, except that the filtrate (B) was kept for several days before treatment for recovery of unchanged 3-amino-4-hydroxyphenylarsinic acid, to allow complete precipitation of 1-thiobenzoxazolone-4-arsinic acid. Products obtained: 1-thiobenzoxazolone-4-arsinic acid (16 g.) (Found for acid dried at 80°: As, 27·2; N, 5·0; S, 11·8. Calc.: As, 27·3; N, 5·1; S, 11·6%); 1-thiobenzoxazolone-4-arsenic disulphide (6 g.) (Found: As, 23·1; N, 4·2; S, 29·6; atomic ratios As : N : S = 1·00 : 0·97 : 3·01. Calc.: As, 25·9; N, 4·8; S, 33·2%); 3-amino-4-hydroxyphenylarsinic acid (unchanged) (6 g.) (Found: As, 32·1; N, 5·9. Calc.: As, 32·2; N, 6·0%); arsenious sulphide (5 g.).

3 : 4-*Diaminophenylarsinic Acid and Potassium Ethyl Xanthate* (*Typical Example*).—Treated exactly as described above, 3 : 4-diaminophenylarsinic acid (46·6 g.) gave the following products: 2-Thiolbenziminazole-5-arsinic acid (15·5 g.) (Found for acid dried at 80°: As, 27·3; N, 10·1; S, 11·8. Calc.: As, 27·4; N, 10·2; S, 11·7%); 2-thiolbenziminazole-5-arsenic disulphide (6 g.) (Found: As, 23·2; N, 8·6; S, 29·7; atomic ratios As : N : S = 1·00 : 1·98 : 3·00. Calc.: As, 26·0; N, 9·7; S, 33·3%); 3 : 4-diaminophenylarsinic acid (unchanged) (6 g.) (Found: As, 32·2; N, 11·9. Calc.: As, 32·2; N, 12·0%); arsenious sulphide (4·5 g.).

RESEARCH LABORATORIES, MESSRS. MAY & BAKER, LTD.,
LONDON, S.W.18.
[*Received, April 10th,* 1930.]