XCVI.—*Trypanocidal Activity and Chemical Constitution. Part I. New Sulphur Derivatives of Aromatic Organic Arsenicals.*

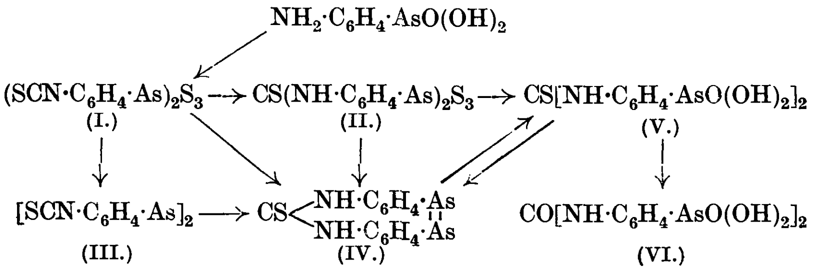
By JOHN GARWOOD EVERETT.

THE observation that neosalvarsan and sulpharsphenamine are more lastingly curative than salvarsan base against experimental infections of *Trypanosoma equiperdum* in mice led to the present research, which was undertaken to determine whether the presence of sulphur in the molecule influences permanency of cure.

Compounds containing the thiocarbonyl group, :C:S, attached to nitrogen were first considered, as these contain an arrangement of nitrogen, carbon, and sulphur atoms similar to that of the side chains of neosalvarsan and sulpharsphenamine, if in these it is assumed that sulphur is attached to carbon, for which view there is some evidence (Newbery and Phillips, J., 1928, 119; Raschig, *Ber.*, 1926, **59**, 859; Binz, *ibid.*, p. 1695). Only three compounds of this type have been previously described, *viz.*, allylthiocarbamyl-*p*-arsanilic acid and its methyl homologue (Thoms, D.R.-P. 294,632) and thiocarbamyl-*p*-arsanilic acid (Morgan, " Organic Compounds of Arsenic and Antimony," p. 162).

In the present instance, aminophenylarsinic acids were condensed with carbon disulphide in presence of alcohol and sodium hydroxide : the thiocarbonyl group entered the amino-group, and the sulphides formed attacked the arsinic acid group, giving thioarsenates, which on acidification yielded amorphous sulphides. From *p*-arsanilic acid, pp′-*dithiocarbiminophenylarsenic sesquisulphide* (I) was obtained instead of the expected diphenylthiourea-*pp′*-arsenic sesquisulphide (II). The constitution of (I) was shown as follows : On hydrolysis with sodium hydroxide it yielded *diphenylthiourea*-pp′-*arsenic sesquisulphide* (II), and on reduction with sodium hyposulphite pp′-*dithiocarbiminoarsenobenzene* (III), completely soluble in 5% sodium hydroxide solution, was obtained. This on hydrolysis with sodium hydroxide gave pp′-*arseno*(*diphenylthiourea*) (IV), insoluble in that reagent and identical with the compound obtained by reduction of the sulphide (II), by simultaneous reduction and hydrolysis of the sulphide (I), and by reduction of *diphenylthiourea*-pp′-*diarsinic acid* (V).

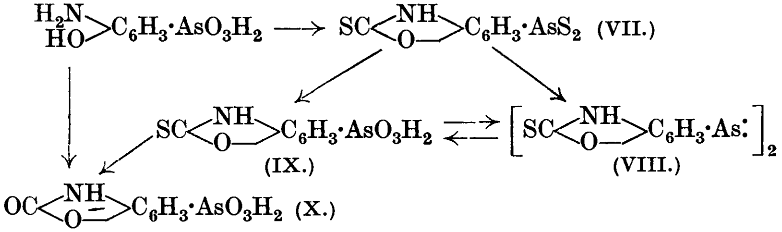
pp′-Arseno(diphenylthiourea) (IV) gave, on treatment with iodine, diphenylthiourea-*pp′*-diarsinic acid (V) identical with that obtained either by iodine oxidation of the sulphide (II) or by treatment of *p*-arsanilic acid with thiocarbonyl chloride; and (V) in presence of excess of sodium bicarbonate reacted further with iodine, giving diphenylurea-*pp′*-diarsinic acid (VI), identical with the substance obtained by the action of carbonyl chloride on *p*-arsanilic acid. These reactions are summarised below. The analogy between the arsenated and the non-arsenated compounds was established by boiling phenylthiocarbimide with sodium hydroxide, complete conversion into thiocarbanilide occurring.



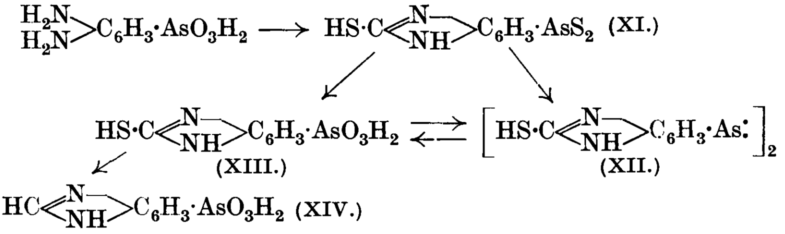
$$\begin{tikzcd}
 & \mathrm{NH_2{\cdot}C_6H_4{\cdot}AsO(OH)_2} \arrow[dl] & \\
\underset{\text{(I.)}}{\mathrm{(SCN{\cdot}C_6H_4{\cdot}As)_2S_3}} \arrow[r] \arrow[d] \arrow[dr] & \underset{\text{(II.)}}{\mathrm{CS(NH{\cdot}C_6H_4{\cdot}As)_2S_3}} \arrow[r] \arrow[d] & \underset{\text{(V.)}}{\mathrm{CS[NH{\cdot}C_6H_4{\cdot}AsO(OH)_2]_2}} \arrow[d] \arrow[dl, shift left] \\
\underset{\text{(III.)}}{\mathrm{[SCN{\cdot}C_6H_4{\cdot}As]_2}} \arrow[r] & \underset{\text{(IV.)}}{\mathrm{CS}{<}\begin{matrix}\mathrm{NH{\cdot}C_6H_4{\cdot}As}\\ \| \\ \mathrm{NH{\cdot}C_6H_4{\cdot}As}\end{matrix}} \arrow[ur, shift left] & \underset{\text{(VI.)}}{\mathrm{CO[NH{\cdot}C_6H_4{\cdot}AsO(OH)_2]_2}}
\end{tikzcd}$$

(Formulæ II and IV are so represented for simplicity. The possibility of more extended ring structure is recognised.)

3-Amino-4-hydroxyphenylarsinic acid gave 1-*thiobenzoxazolone-4-arsenic disulphide* (VII), which on reduction with sodium hyposulphite gave 4 : 4′-*arseno-*(1-*thiobenzoxazolone*) (VIII). This arseno-compound and the disulphide (VII), on treatment with iodine, both yielded 1-*thiobenzoxazolone-4-arsinic acid* (IX) identical with that obtained by treating 3-amino-4-hydroxyphenylarsinic acid with thiocarbonyl chloride. This acid (IX) in presence of excess of sodium bicarbonate reacted further with iodine, giving benzoxazolone-4-arsinic acid (X) identical with the acid obtained by the action of carbonyl chloride on 3-amino-4-hydroxyphenylarsinic acid. These reactions are summarised as follows :



3:4-Diaminophenylarsinic acid gave 2-*thiolbenziminazole-5-arsenic disulphide* (XI), and steps similar to the above were taken to prove its constitution : the results are shown below. 2-*Thiolbenziminazole-5-arsinic acid* (XIII) on oxidation with iodine in presence of sodium bicarbonate gave *benziminazole-5-arsinic acid* (XIV), no trace of 2 : 3-dihydrobenziminazolone-5-arsinic acid being detected.



From the above facts it is clear that, in the compounds mentioned, sulphur attached to arsenic only (sulphide sulphur) may be sharply differentiated from sulphur attached to carbon or carbon and hydrogen only (mercaptan sulphur) by means of either sodium hyposulphite or iodine, the mercaptan sulphur not being oxidised by iodine unless sodium bicarbonate (or some other alkali) is present. Further, the three arsinic acids (V), (IX), and (XIII) gave no colour with an alkaline solution of sodium nitroprusside, whereas all the sulphides mentioned gave a deep violet colour with this reagent.

With a view to a comparison of oxygen with sulphur in analogous compounds, diphenylurea-*pp′*-diarsinic acid (VI), benzoxazolone-4-arsinic acid (X), and 2 : 3-*dihydrobenziminazolone*-5-*arsinic acid* were prepared and reduced to the corresponding arseno-compounds.

Therapeutic Results.—The above-mentioned thiocarbonyl compounds and their carbonyl analogues have been tested against an experimental infection of *T. equiperdum* in mice with the following results, which amount to a direct comparison of sulphur with oxygen : T = maximum tolerated dose in mg./g. of mouse, c = minimum curative dose in mg./g. of mouse, r = number of days elapsing between cure and reappearance of trypanosomes in the peripheral blood-stream, i = intravenous, and o = oral.

Thiocarbonyl compounds.		*T*.	*c*.	*T*/*c*.	*r*.
pp′-Dithiocarbiminophenylarsenic sesquisulphide (I)	*i*	0·05	0·05	1·0	13
	o	3·0	>3·0	nil	
Diphenylthiourea-*pp′*-arsenic sesquisulphide (II)	*i*	0·01	0·01	1·0	4
	o	2·0	2·0	1·0	12
2-Thiolbenziminazole-5-arsenic disulphide (XI)	*i*	0·05	0·006	8·0	>30
	o	10·0	0·2	50·0	14
1-Thiobenzoxazolone-4-arsenic disulphide (VII)	*i*	0·02	0·02	1·0	6
	o	1·0	>1·0	nil	
pp′-Dithiocarbiminoarsenobenzene (III)	*i*	0·025	0·02	1·0	20
	o	2·0	0·7	3·0	7
pp′-Arseno(diphenylthiourea) (IV)	*i*		insoluble		
	o	>10·0	3·0	>3·0	15
5 : 5′-Arseno-(2-thiolbenziminazole) (XII)	*i*	0·1	0·005	20·0	>30
	o	>10·0	0·05	>200·0	12
4 : 4′-Arseno-(1-thiobenzoxazolone) (VIII)	*i*	0·07	0·05	1·5	1
	o	4·0	2·0	2·0	10
Diphenylthiourea-*pp′*-diarsinic acid (V)	*i*	0·6	>0·6	nil	
	o	9·0	1·0	9·0	20
2-Thiolbenziminazole-5-arsinic acid (XIII)	*i*	0·5	0·5	1·0	>30
	o	10·0	0·1	100·0	15
1-Thiobenzoxazolone-4-arsinic acid (IX)	*i*	1·0	1·0	1·0	10
	o	0·8	0·8	1·0	10
Carbonyl compounds.					
pp′-Arsenodiphenylurea	*i*	insoluble			
	o	>10·0	4·0	>3·0	6
5 : 5′-Arseno-(2 : 3-dihydrobenziminazolone)	*i*	insoluble			
	o	8·0	0·05	170·0	10
4 : 4′-Arsenobenzoxazolone	*i*	0·05	0·025	2·0	1
	o	4·0	3·0	1·3	8
Diphenylurea-*pp′*-diarsinic acid (VI)	*i*	2·0	>2·0	nil	
	o	16·0	2·0	8·0	12
2 : 3-Dihydrobenziminazolone-5-arsinic acid	*i*	0·6	0·3	2·0	6
	o	16·0	0·1	160·0	7
Benzoxazolone-4-arsinic acid (X)	*i*	1·0	0·5	2·0	12
	o	1·0	0·1	10·0	10

Conclusions.—(1) From the last column it is seen that permanency of cure is not appreciably influenced by the substitution of sulphur for oxygen, except in the case of those compounds containing arsenic in the 5-position in a 2-thiolbenziminazole ring, which are outstandingly efficacious.

(2) Considering the results as a whole, it is evident that the substitution of sulphur for oxygen in these compounds causes no appreciable difference in either toxicity or therapeutic activity, and this is of interest since it has already been shown (King and Murch, J., 1925, **127**, 2632; King, Hewitt, and Murch, J., 1926, 1355; Durham, Marchal, and King, *J. Pharm. Exp. Ther.*, 1926, **28**, 341) that the substitution of sulphur for carbon in another series of arsenicals destroys trypanocidal activity *in vivo*, the groups compared in this case being $SO_2{\cdot}NH$ (sulphonamide) and $CO{\cdot}NH$ (carbonamide).

EXPERIMENTAL.

[In many cases where the percentages of arsenic, nitrogen, and sulphur found are rather widely divergent from the theoretical values, ordinary criteria of purity are inapplicable owing to the amorphous nature of the compounds. The atomic ratios found for the same compound obtained in different ways are, however, satisfactory. To justify reliance on these values, C, H, S, N, As ratios have been determined in one case, that of 4 : 4′-arseno-(1-thiobenzoxazolone).]

pp′-*Dithiocarbiminophenylarsenic Sesquisulphide* (I).—*p*-Arsanilic acid (22 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 residue was dissolved in warm water and acidified (Congo-red) with hydrochloric acid. The precipitated *sesquisulphide* was dissolved in boiling sodium carbonate solution (20%), treated with charcoal, again precipitated, and treated with carbon disulphide to remove free sulphur (yield, 18 g.; 70%) (Found: As, 25·0; N, 4·6; S, 26·3; atomic ratios As : N : S = 2·00 : 1·97 : 4·94. $C_{14}H_8N_2S_5As_2$ requires As, 29·2; N, 5·5; S, 31·1%). It was obtained as a light yellow, amorphous solid insoluble in water, acids, or organic solvents, but soluble in excess of cold sodium hydroxide solution or in excess of boiling sodium carbonate solution.

The two following disulphides were prepared similarly and had similar physical properties: 1-*Thiobenzoxazolone*-4-*arsenic disulphide* (VII), from 3-amino-4-hydroxyphenylarsinic acid (yield, 64%) (Found: As, 22·0; N, 4·0; S, 28·2; atomic ratios As : N : S = 1·00 : 0·97 : 3·02. $C_7H_4ONS_3As$ requires As, 25·9; N, 4·8; S, 33·2%), is soluble in dilute solutions of sodium cyanide: this is a characteristic property of 1-thiobenzoxazolone. 2-*Thiolbenziminazole*·5-*arsenic disulphide* (XI), from 3 : 4-diaminophenylarsinic acid (yield, 64%) (Found: As, 20·8; N, 7·8; S, 26·9; atomic ratios As : N : S = 1·00 : 2·00 : 3·03. $C_7H_5N_2S_3As$ requires As, 26·0; N, 9·7; S, 33·3%).

Diphenylthiourea·pp′-*arsenic sesquisulphide* (II) was obtained, by boiling *pp*′-dithiocarbiminophenylarsenic sesquisulphide (10 g.) for 6 hours with sodium hydroxide solution (25%, 50 c.c.), and acidifying the cooled solution (Congo-red) with hydrochloric acid, as a light yellow, amorphous solid resembling (I) in solubility (Found: As, 28·4; N, 5·2; S, 24·5; atomic ratios As : N : S = 1·00 : 0·98 : 2·02. $C_{13}H_{10}N_2S_4As_2$ requires As, 31·8; N, 5·9; S, 27·1%).

pp′-*Dithiocarbiminoarsenobenzene* (III).—*pp*′-Dithiocarbiminophenylarsenic sesquisulphide (30 g.) was mixed with water (300 c.c.) and just sufficient sodium hydroxide to effect solution. Sodium hyposulphite (375 g.) and sodium hydroxide (7·5 g.) were dissolved in water (3 l.). The two solutions were mixed and kept at 55° for 1 hour. The precipitated *arseno-compound*, after being washed with water and dried in a vacuum over concentrated sulphuric acid, was obtained as a light yellow, amorphous solid, soluble in 5% sodium hydroxide solution (yield, 18 g.; 74%) (Found: As, 33·7; N, 6·2; S, 14·35; atomic ratios As : N : S = 1·00 : 0·99 : 0·99. $C_{14}H_8N_2S_2As_2$ requires As, 35·9; N, 6·7; S, 15·3%).

(Unless otherwise stated, reduction with sodium hyposulphite was carried out as above.)

pp′-*Arseno*(*diphenylthiourea*) (IV).—(1) *pp*′-Dithiocarbiminophenylarsenic sesquisulphide was reduced with sodium hyposulphite as described above, except that sodium hydroxide solution (25%; 100 c.c.) was added, and the temperature kept at 90° (yield, 40%) (Found: As, 34·4; N, 6·2; S, 8·0; atomic ratios As : N : S = 2·00 : 1·92 : 1·08. $C_{13}H_{10}N_2SAs_2$ requires As, 39·9; N, 7·4; S, 8·5%).

(2) Diphenylthiourea-*pp*′-arsenic sesquisulphide was reduced with sodium hyposulphite (yield, 62%) (Found: As, 35·0; N, 6·4; S, 8·1%; atomic ratios As : N : S = 2·00 : 1·96 : 1·08).

(3) Diphenylthiourea-*pp*′-diarsinic acid was reduced with sodium hyposulphite (yield, 71%) (Found: As, 36·3; N, 6·7; S, 7·9%; atomic ratios As : N : S = 2·00 : 1·98 : 1·02).

(4) A solution of *pp*′-dithiocarbiminoarsenobenzene (4 g.) in sodium hydroxide solution (20%; 100 c.c.) was boiled for 15 minutes and the precipitate was removed, washed with water, and dried in a vacuum over sulphuric acid (yield, 3 g.; 81%) (Found: As, 36·5; N, 6·8; S 7·8%; atomic ratios As : N : S = 2·00 : 1·98 : 1·00).

pp′·*Arseno*(*diphenylthiourea*) was obtained by these four methods as an orange, amorphous solid insoluble in sodium hydroxide.

4 : 4′-*Arseno*-(1-*thiobenzoxazolone*) (VIII).—(1) 1-Thiobenzoxazolone-4·arsenic disulphide was reduced with sodium hyposulphite (yield, 73%) (Found: C, 33·6, 33·2; H, 2·5, 2·3; N, 5·7, 5·8; S, 13·4, 13·6; As, 31·0, 31·3; atomic ratios C : H : N : S : As = 6·8 : 5·7 : 0·99 : 1·02 : 1·00. $C_{14}H_8O_2N_2S_2As_2$ requires C, 37·4; H, 1·8; N, 6·2; S, 14·2; As, 33·3%). The loss in a vacuum over sulphuric acid was 1·8% and ash 3%.

(2) 1-Thiobenzoxazolone-4-arsinic acid was reduced with sodium hyposulphite (yield, 70%) (Found: As, 32·0; N, 6·1; S, 13·9%; atomic ratios As : N : S = 1·00 : 1·02 : 1·02).

4 : 4′-*Arseno*-(1-*thiobenzoxazolone*) obtained by these two methods was a light yellow, amorphous powder, soluble in sodium hydroxide solution and very readily soluble in dilute solutions of sodium cyanide.

5 : 5′·*Arseno*-(2-*thiolbenziminazole*) (XII).—(1) 2·Thiolbenziminazole-5-arsenic disulphide was reduced with sodium hyposulphite (yield, 72%) (Found: As, 30·0; N, 11·2; S, 12·9; atomic ratios As : N : S = 1·00 : 2·01 : 1·01. $C_{14}H_{10}N_4S_2As_2$ requires As, 33·5; N, 12·5; S, 14·3%).

(2) Thiolbenziminazole-5-arsinic acid was reduced with sodium hyposulphite (yield, 68%) (Found: As, 30·7; N, 11·5; S, 13·1%; atomic ratios As : N : S = 1·00 : 2·01 : 1·01).

5 : 5′-*Arseno*-(2-*thiolbenziminazole*) obtained by these two methods was a light yellow, amorphous powder, readily soluble in dilute solutions of sodium hydroxide.

pp′-*Arseno*(*diphenylurea*) was obtained as an orange amorphous powder, insoluble in sodium hydroxide solution, by reduction of diphenylurea-*pp*′-diarsinic acid with sodium hyposulphite (yield, 80%) (Found: As, 36·0; N, 6·6; atomic ratio As : N = 1·00 : 0·98. $C_{13}H_{10}ON_2As_2$ requires As, 41·6; N, 7·8%).

4 : 4′-Arsenobenzoxazolone was prepared by Fargher's method (J., 1919, **115**, 991) and obtained as a light yellow, amorphous powder, soluble in sodium hydroxide solution (Found: As, 31·5; N, 5·9; atomic ratio As : N = 1·00 : 1·00. Calc.: As, 35·7; N, 6·7%).

5 : 5′-*Arseno*-(2 : 3-*dihydrobenziminazolone*) was obtained as a yellow, amorphous powder, insoluble in sodium hydroxide solution, by reduction of 2 : 3-dihydrobenziminazolone-5-arsinic acid with sodium hyposulphite (yield, 85%) (Found: As, 33·2; N, 12·5; atomic ratio As : N = 1·00 : 2·01. $C_{14}H_{10}O_2N_4As_2$ requires As, 36·1; N, 13·5%).

Diphenylthiourea-pp′-*diarsinic Acid* (V).—(1) Thiocarbonyl chloride (6 g.) was added gradually with vigorous shaking to *p*-arsanilic acid (22 g.) dissolved in *N*-sodium hydroxide (180 c.c.), alkalinity being maintained by the addition of sodium hydroxide solution (20%) as required. The filtered solution, after treatment with charcoal, was acidified (Congo-red) with hydrochloric acid and the diarsinic acid obtained was dissolved in sodium bicarbonate solution, reprecipitated, and finally recrystallised from 50% alcohol (yield, 17 g.; 69%) (Found on acid dried at 80° : As, 31·5; N, 5·8; S, 6·8. $C_{13}H_{14}O_6N_2SAs_2$ requires As, 31·5; N, 5·9; S, 6·7%).

(2) *pp'*-Arseno(diphenylthiourea) (3·8 g.) was stirred with water (20 c.c.), and *N*/10-iodine added gradually until no more was absorbed (500 c.c.). A solution of the precipitate in aqueous sodium bicarbonate (6%; 60 c.c.) was treated with charcoal, filtered, and acidified (Congo-red) with hydrochloric acid (yield, 2 g.; 42%) (Found on acid dried at 80° : As, 31·4; N, 5·8; S, 6·7%).

(3) Diphenylthiourea-*pp'*-arsenic sesquisulphide (4·7 g.) was stirred with water (20 c.c.), and *N*/10-iodine added (300 c.c.). The precipitate was treated as described under (2) (yield, 1·5 g.; 31%) (Found on acid dried at 80° : As, 31·4; N, 5·7; S, 6·8%).

Diphenylthiourea-pp'-*diarsinic acid* was thus obtained in rosettes of fine pale yellow needles. It is insoluble in cold water or dilute mineral acids, sparingly soluble in hot water, and moderately easily soluble in warm alcohol. The calcium and magnesium salts are amorphous and the barium salt is micro-crystalline.

2-*Thiolbenziminazole*-5-*arsinic acid* (XIII) was obtained (1) from 3 : 4-diaminophenylarsinic acid (23 g.) and thiocarbonyl chloride (12 g.) as described under diphenylthiourea-*pp'*-diarsinic acid, excluding the final recrystallisation from alcohol (yield, 21 g.; 78%) (Found on acid dried at 80° : As, 27·3; N, 10·2; S, 11·8. $C_7H_7O_3N_2SAs$ requires As, 27·4; N, 10·2; S, 11·7%), (2) from 5 : 5'-arseno-(2-thiolbenziminazole) (4·5 g.) and *N*/10-iodine (500 c.c.) as described under diphenylthiourea-*pp'*-diarsinic acid (yield, 2 g.; 36%) (Found on acid dried at 80° : As, 27·3; N, 10·1; S, 11·6%), and (3) from 2-thiolbenziminazole-5-arsenic disulphide (2·9 g.) and *N*/10-iodine (200 c.c.) as described under diphenylthiourea-*pp'*-diarsinic acid (yield, 1 g.; 37%) (Found on acid dried at 80° : As, 27·3; N, 10·1; S, 11·8%).

The arsinic acid was obtained by these three methods in small buff needles, insoluble in cold water or dilute mineral acids, moderately easily soluble in hot water, and readily soluble in warm alcohol. The calcium salt forms rosettes of needles, and the barium salt fine needles; the magnesium salt is amorphous.

1-*Thiobenzoxazolone*-4-*arsinic acid* (IX) was obtained (1) from 3-amino-4-hydroxyphenylarsinic acid as described under 2-thiolbenziminazole-5-arsinic acid (yield, 78%) (Found on acid dried at 80° :

As, 27·3; N, 5·1; S, 11·7. $C_7H_6O_4NSAs$ requires As, 27·3; N, 5·1; S, 11·6%), (2) from 4 : 4′-arseno-(1-thiobenzoxazolone) as described under 2-thiolbenziminazole-5-arsinic acid (yield, 45%) (Found on acid dried at 80° : As, 27·2; N, 5·1; S, 11·7%), and (3) from 1-thiobenzoxazolone-4-arsenic disulphide as described under 2-thiolbenziminazole-5-arsinic acid (yield, 30%) (Found on acid dried at 80° : As, 27·2; N, 5·0; S, 11·8%). It formed small, pale yellow needles, insoluble in cold water or dilute mineral acids, sparingly soluble in hot water, and moderately easily soluble in warm alcohol. The magnesium salt is amorphous.

Diphenylurea-pp′-*diarsinic Acid* (VI).—This was obtained (1) from *p*-arsanilic acid and carbonyl chloride, essentially as described in D.R.-P. 191548 (Found on acid dried at 80° : As, 32·5; N, 6·0. Calc.: As, 32·6; N, 6·1%), and (2) from diphenylthiourea-*pp*′-diarsinic acid (2·4 g.), dissolved in water (60 c.c.) and sodium bicarbonate (20 g.), and *N*/2-iodine (40 c.c.). The colourless solution, after treatment with charcoal, was filtered and acidified (Congo-red) with hydrochloric acid; the precipitated acid was dissolved in sodium bicarbonate solution and reprecipitated (yield, 1 g.; 43%) (Found on acid dried at 80° : As, 32·7; N, 6·1%).

Diphenylurea-*pp*′-diarsinic acid forms small white needles, insoluble in cold water or dilute mineral acids, sparingly soluble in hot water or alcohol. The calcium and magnesium salts are amorphous; the barium salt forms rosettes of small prisms.

Benzoxazolone-4-arsinic acid (X), obtained (1) by Fargher's method (*loc. cit.*) (Found on acid dried at 80° : As, 28·9; N, 5·4. Calc.: As, 29·0; N, 5·4%) and (2) from 1-thiobenzoxazolone-4-arsinic acid (2·75 g.) and *N*/2-iodine (80 c.c.) as described under diphenylurea-*pp*′-diarsinic acid (yield, 2 g.; 77%) (Found on acid dried at 80° : As, 28·6; N, 5·2%), formed prismatic needles, insoluble in cold water or dilute mineral acids and readily soluble in hot water or alcohol.

2 : 3-Dihydrobenziminazolone-5-arsinic acid, obtained from 3 : 4-diaminophenylarsinic acid and carbonyl chloride essentially as described by Bertheim (*Ber.*, 1911, **44**, 3097) (Found on acid dried at 80° : As, 29·0; N, 10·7. Calc.: As, 29·1; N, 10·8%), formed small prisms, insoluble in cold water or dilute mineral acids and sparingly soluble in hot water or alcohol. The calcium salt crystallised in feathery needles, the magnesium salt in rosettes of fine needles, and the barium salt in large plates.

Benziminazole-5-arsinic acid (XX), obtained from 2-thiolbenziminazole-5-arsinic acid (1·4 g.) and *N*/2-iodine (40 c.c.) as described under diphenylurea-*pp*′-diarsinic acid (yield, 1 g.; 83%) (Found on acid dried at 80° : As, 31·0; N, 11·6 Calc.: As, 31·0; N, 11·5%), formed rosettes of needles, insoluble in cold water, sparingly soluble in hot water or alcohol, and readily soluble in dilute mineral acids. The magnesium salt is amorphous and the barium and calcium salts are microcrystalline (compare Baxter and Fargher, J., 1919, **115**, 1372; Phillips, J., 1928, 3137).

Conversion of Phenylthiocarbimide into Thiocarbanilide.—The thiocarbimide (10 g.) was boiled under reflux for 1 hour with sodium hydroxide solution (20%; 100 c.c.). The resulting thiocarbanilide was removed, washed with water, and recrystallised from hot alcohol (yield, 8·0 g.; 94%). M. p. 153° (alone or mixed with an authentic specimen).

MESSRS. MAY & BAKER, LTD.,
WANDSWORTH, S.W. 18.

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