PART V

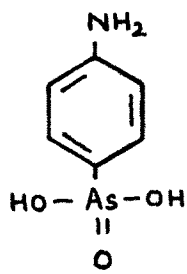
Interaction of atoxyl with halogen derivatives of (a) acetoacetarylamides and (b) cyanacetarylamides-(Synthesis of organo-arsenicals).

PART V

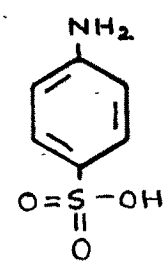
THEORETICAL

The credit of preparing the first aromatic compound of arsenic goes to Be'champ (1). On heating aniline with arsenic acid, he obtained a colourless product, which had the functions of a monobasic acid, giving rise to well defined metallic salts, which are not hydrolysed by aqueous caustic potash.

Ehrlich and Bertheiµm (2) showed that the action of arsenic acid on aniline is comparable with that of sulphuric acid on the same base. In both the cases the acidic group enters the aromatic nucleus giving rise to p-amino-phenyl-arsonic acid (arsanilic acid, I) and p-amino-phenyl-sulphonic acid (sulphanilic acid, II) respectively.

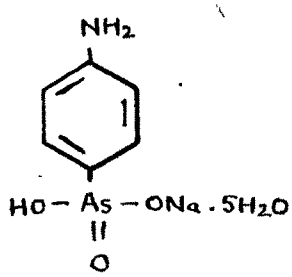


(I)

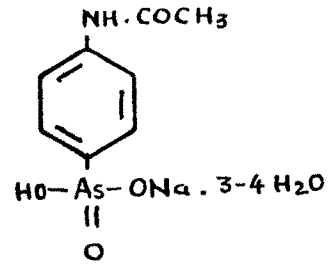


(II)

The recognition of the correct constitution of atoxyl (III)- the monosodium salt of (I), proved to be of utmost importance to chemotherapy, as it opened a wide field for chemical and biological investigations. Ehrlich and Bertheim (2) prepared a large number of new compounds, among the first of which was 4-acetylaminophenyl-arsonic acid, whose sodium salt- arsacetin (IV) is found to be less toxic than (III).



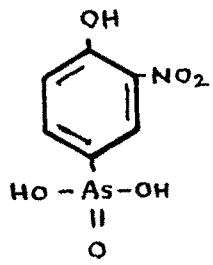
(III)



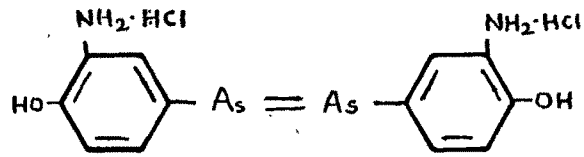
(IV)

Atoxyl and arsacetin showed no trypanocidal properties in the test-tube, but exerted a therapeutic action when injected into the body. Ehrlich found that many tissues act as reducing substances, and he assumed that pentavalent arsenicals, probably, undergo reduction in animal body before acting upon the trypanosomes. Accordingly, he reduced the arsonic acid to arseno compounds by means of suitable reducing agents and found that the products were stronger trypanocidal agents.

Further, in the chemotherapeutic study of azo-dyes, Ehrlich noted that compounds, having the hydroxyl and amino groups in ortho position to each other, were the most active in destroying trypanosomes. He, with his coworkers, prepared a number of compounds of this type viz. 4-oxalyl-aminophenylarsonic acid, 3-nitro-4-oxalylaminophenyl-arsonic acid, 3-nitro-4-aminophenylarsonic acid and 3-nitro-4-hydroxyphenylarsonic acid (V). On reduction of (V) with sodium hydrosulphite, 3,3'-diamino-4,4'-dihydroxyarsenobenzene was obtained, and its dihydrochloride salt (Salvarsan, VI-606) proved to be the best medicament in the treatment of syphilis (3).

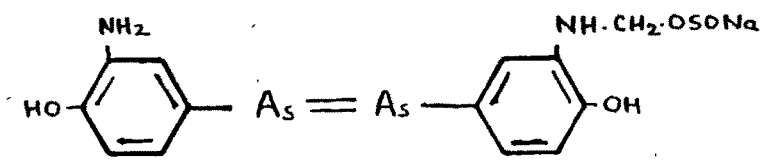


(V)



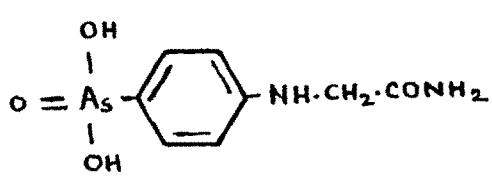
(VI)

Ehrlich and his coworkers, further, in their search for still more biologically effective remedies, prepared numerous derivatives of organo-arsenicals. The most important compound they found was sodium 3,3'-diamino-4,4'-dihydroxy-arsenobenzene-N-methylenesulphinate (neosalvarsan-VII-914) (4).



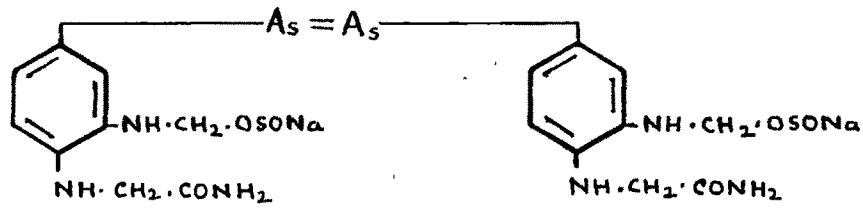
(VII)

Jacobs and Heidelberger (5) by the interaction of atoxyl with chloracetamide, prepared N-(phenyl-4-arsonic acid) glycineamide (Tryparsamide-VIII) which is less toxic than atoxyl.



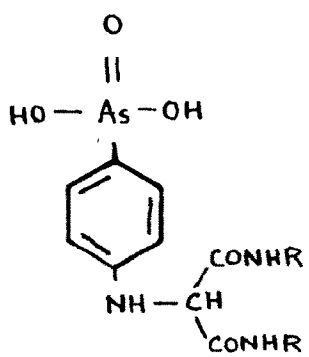
(VIII)

Lewis and Bent (6) with a view to combine the structural features of important drugs, viz., neosalvarsan and tryparsamide prepared sodium formaldehyde sulphoxylate derivative of 3,3'-diamino-4,4'-di-N-glycylamide arsenobenzene (IX), a possible arsenical drug. Certain other substances of this type were tested pharmacologically by them.

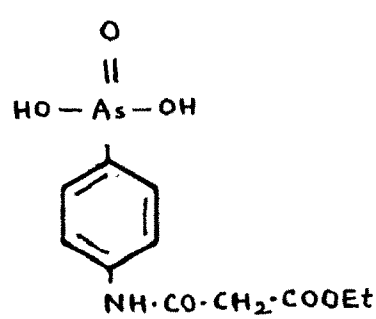


(IX)

Joseph Kennedy (7) prepared p-arsanilic acid derivatives of N-substituted malonamides of the type (X) by condensing the appropriate bromomalonamide with p-arsanilic acid. In physiological tests, the compound, having R=H, was found curative in large doses. Morgan and Walton (8) condensed p-arsanilic acid with carbethoxyacetylchloride and obtained ethyl-p-arsonomalonanilate (XI).

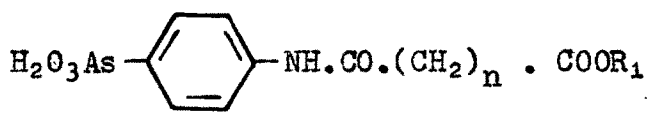


(X) ; (R=H)

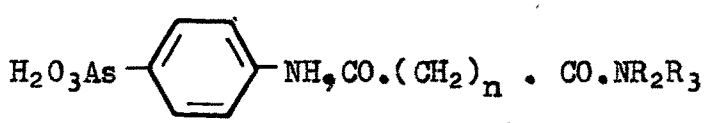


(XI)

Furthermore, Morgan and Walton (9) prepared methyl-p-arsonopimelanilate (XII) where n=5, R_1=Me), and methyl-p-arsonosuberanilate (XII, where n=6, R_1=Me) by condensing the acid chlorides of methyl hydrogen pimelate and methyl hydrogen suberate respectively with atoxyl. The above products when treated with various amines gave amides of the type (XIII) (n = 5 and 6).



(XII)



(XIII)

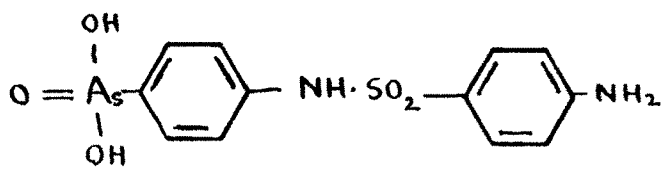
Sodium succinanilomethylamide-p-arsonate (XIII, n = 2 ; R_2 = H ; R_3 = Me) a highly active substance, was tried against both neurosyphilis and sleeping sickness.

R.L.Mcgeachin (10) prepared N-2, 4-dinitro-phenylarsanilic acid by heating p-arsanilic acid and 2,4-dinitro-chlorobenzene with sodium acetate and calcium carbonate. Further, Mcgeachin and Greenwald (11) for the study of the preparation of homologs and analogs of tryparsamide, condensed α-bromopropionic and β-Bromopropionic acids with p-arsanilic acid and obtained N-(4-arsonophenyl)-α-aminopropionic acid and N-(4-arsonophenyl)-β-aminopropionic acid respectively.

Banks et al. (12) found that ~~when~~ cyanogen bromide when treated with p-arsanilic acid under neutral conditions,

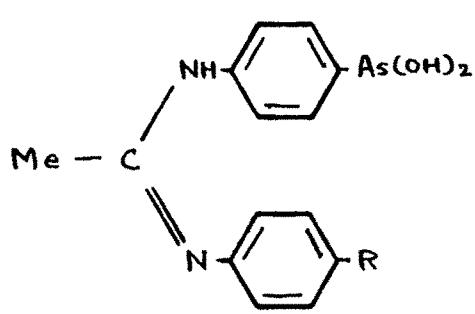
hydrobromic acid was produced and a reaction product of the composition $NCNH.C_6H_4.ASO_3H_2$ was isolated.

Krishnan, Iyar and Guha (13) carried out the reaction of atoxyl with $p\text{-}AcNHC_6H_4SO_2Cl$ and obtained p-(p-acetamidophenylsulphonamido-)-benzenarsonic acid, which, on deacetylation with HCl, gave p(p-aminophenylsulphonamido)-benzenearsonic acid (XIV).

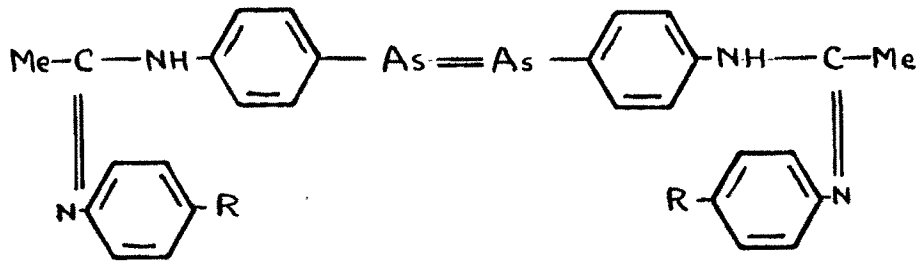


(XIV)

Pathak and Ghosh (14) condensed p-arsanilic acid with acetanilide in presence of $POCl_3$, and obtained compound (XV ; R = H), which was further reduced by hypophosphorus acid in presence of a trace of potassium iodide to give the arseno derivative of the type (XVI, R = H). Similarly, using aceto-p-phenetidine with PCl_3, the same types of compounds were obtained.



(XV)



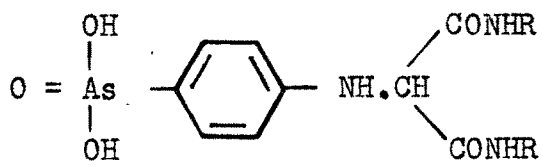
(XVI)

B.Pathak (15) also prepared some 1:4-di-substituted piperizine derivatives containing pentavalent arsenic as possible filaricides.

G.M.Borodina (16) reported the condensation of p-arsanilic acid with 8-(-chloromethyl) caffeine in ethyl alcohol in presence of NaOH giving N-8-(caffeylmethyl)-4-aminophenylarsonic acid.

Kaushiva (17) studied the amoebicidal activity of p-arsanilic acid derivatives of thiozole and thiazolidone prepared by Kaushiva and Pujari (18).

Naik, Trivedi and Mehta (19) studied the interaction of atoxyl with halogen derivatives of some malon arylamides. They observed that even under varying experimental conditions atoxyl did not react with dichloro derivatives of malon arylamides due to the comparative lesser lability of chlorine atoms towards atoxyl. However, it has been found that the bromine atom, substituting the hydrogen atom of the reactive methylene group (-CHBr-) reacted with atoxyl easily, and the compounds of the type (XVII) were obtained by condensing atoxyl with mono bromo malon arylamides.

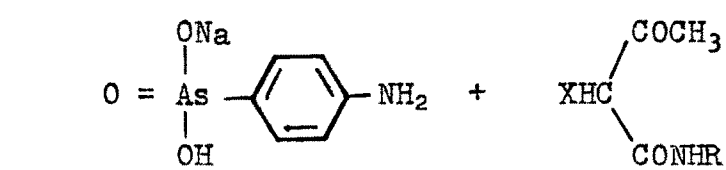


(XVII)

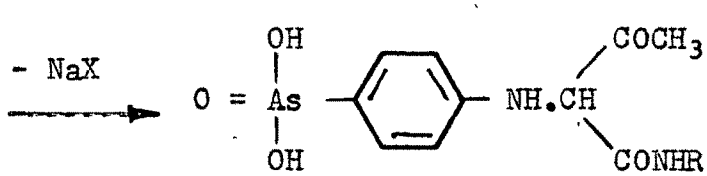
(Where R = C_6H_4Br or $C_6H_4CH_3$ or $C_6H_5CH_2$)

Taking into considerations all these factors it was proposed to study the interactions of atoxyl separately with mono halogen derivatives of the substituted amides of acetoacetic acid and those of cyanacetic acid.

In the present investigation atoxyl (a) is allowed to react with the respective (i) (mono) chloro-bromo- and iodo derivatives of acetoacet arylamides (b), as well as with (ii) (mono) bromo-and iodo derivatives of cyanacet arylamides (c). In each of the above cases, the halogen atom of the amide reacted with a hydrogen atom of the amino group of atoxyl to give p-arsonoanilino acetoacet arylamides (XVIII) and p-arsonoanilinocyanacet arylamides (XIX) prepared by Mehta and Trivedi (20). Thus,

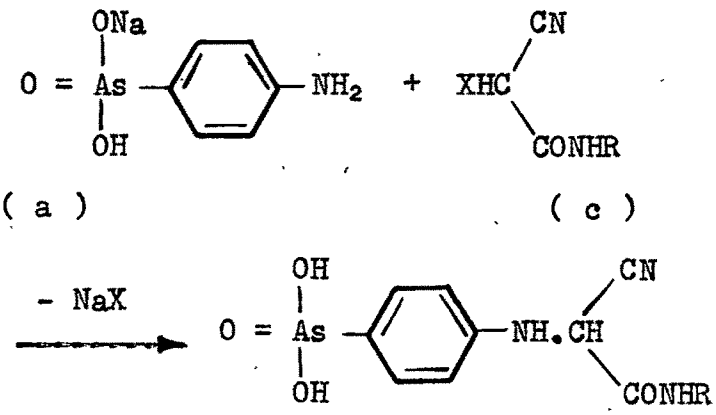


(a) (b)



(XVIII)

(ii)



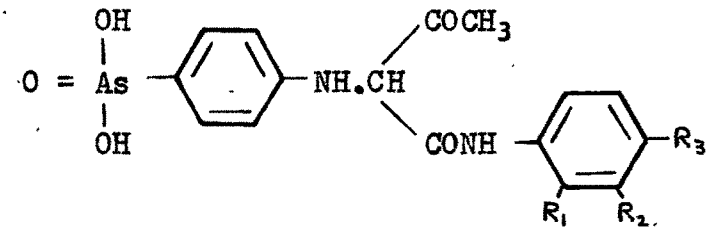
(a) (c)

(XIX)

(Where X = chloride,bromide or iodide radical, R = phenyl, tolyl,xylyl or naphthyl radical).

Mono halogen derivative of acetoacet arylamide (0.01 M) or of cyanacet arylamide (0.01 M), was dissolved in minimum quantity of ethyl alcohol. Atoxyl (0.01 M) dissolved in 5 ml. of water was added to it. The reaction mixture was then refluxed on a sand bath for three hours in the case of chloro-or bromo derivatives ; while for half an hour in case of iodo derivatives of the respective amides. The mixture on cooling, gave the crude product, which, after charcoaling, was crystallised from aqueous alcohol in the form of tiny clusters.

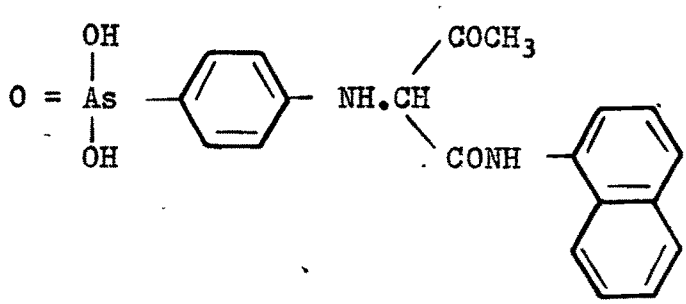
Thus, by the interaction of atoxyl with the respective mono-halogen derivatives of acetoacetarylamides as well as with monobromo and monoiodo derivatives of cyanacet arylamides, the p-arsonoanilino derivatives of acetoacet arylamides and those of cyanacet arylamides, which are given below, have been prepared.



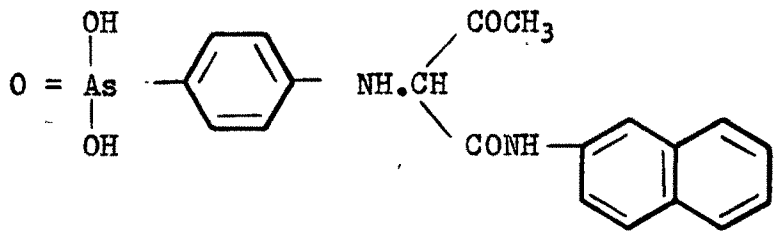
(A)

p-Arsonoanilino derivatives of acetoacet arylamides.

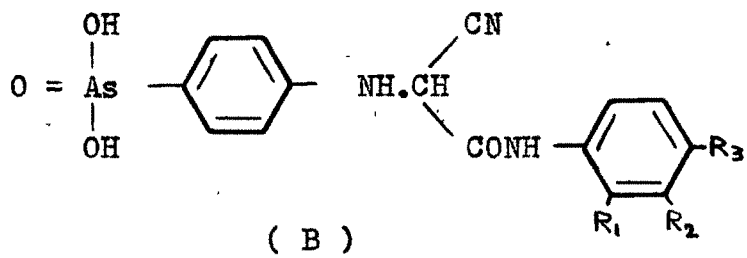
1. p-Arsonoanilino acetoacet anilide
   (A, $R_1=R_2=R_3=H$)
2. p-Arsonoanilino acetoacet-p-chloroanilide
   (A, $R_1=R_2=H$; $R_3=Cl$)
3. p-Arsonoanilino acetoacet-o-toluidide
   (A, $R_2=R_3=H$; $R_1=CH_3$)
4. p-Arsonoanilino acetoacet-p-toluidide
   (A, $R_1=R_2=H$; $R_3=CH_3$)
5. p-Arsonoanilino acetoacet-1:2:4-xylidide
   (A, $R_2=H$; $R_1=R_3=CH_3$)
6. p-Arsonoanilino acetoacet-1:3:4-xylidide
   (A, $R_1=H$; $R_2=R_3=CH_3$)
7. p-Arsonoanilino acetoacet-p-phenitidide
   (A, $R_1=R_2=H$; $R_3=OC_2H_5$)
8. p-Arsonoanilino acetoacet-α-naphthylamide



9. p-Arsonoanilino acetoacet-β-naphthylamide



p-Arsonoanilino derivatives of cyanacet arylamides



(B)

1. p-Arsonoanilino cyanacet anilide

   (B, $R_1=R_2=R_3=H$)

2. p-Arsonoanilino cyanacet-o-toluidide

   (B, $R_2=R_3=H$; $R_1=CH_3$)

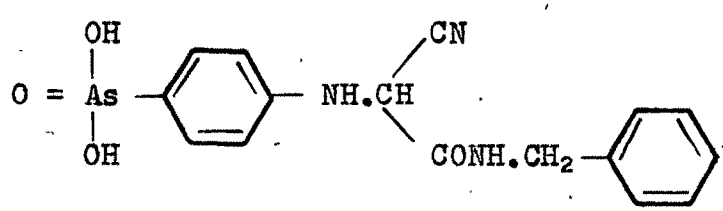
3. p-Arsonoanilino cyanacet-m-toluidide

   (B, $R_1=R_3=H$; $R_2=CH_3$)

4. p-Arsonoanilino cyanacet-p-toluidide

   (B, $R_1=R_2=H$; $R_3=CH_3$)

5. p-Arsonoanilino cyanacet-benzylamide



6. p-Arsonoanilino cyanacet-o-anisidide

   (B, $R_2=R_3=H$; $R_1=OCH_3$)

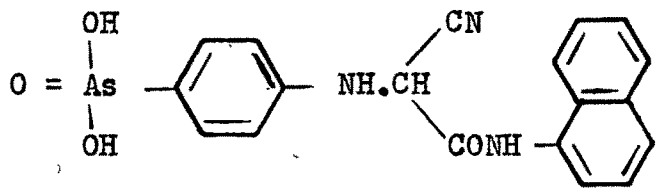
7. p-Arsonoanilino cyanacet-p-phenitidide

   (B, $R_1=R_2=H$; $R_3=OC_2H_5$)

8. p-Arsonoanilino cyanacet-1:3:4-xylidide

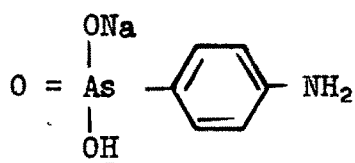
(B, R_1=H ; R_2=R_3=CH_3)

9. p-Arsonoanilino cyanacet-α-naphthylamide



That the p-arsonoanilino compounds have the structures as represented above follows from the considerations given below :-

(i) The linkage between the halogen derivatives and atoxyl may be either at the oxygen atom, which was originally one of the hydroyl groups in the following as underlined,



or, the hydrogen replaced may be one of the hydrogen atoms forming the amino grouping.

(ii) Experimental evidence shows that all the derivatives prepared here, have no primary amino group and that the original amino grouping has been converted into - NH - grouping.

Evidence to show that the above compounds have no amino - NH_2 - grouping

The compound, obtained by the interaction of atoxyl and mono halogen derivative of acetoacetarylamide

or cyanacet arylamide, was dissolved in hydrochloric acid and little alcohol. It was then treated with - $NaNO_2$ - sodium nitrite - and alkaline - β- naphthol by immersing the test tube in ice-cold water, a test for diazo reaction-, to note the presence of the amino- NH_2 - grouping. It did not give the characteristic colour ; but only a clear yellowish solution was obtained, which showed that amino - NH_2 - grouping was absent. Similarly all the above compounds were tested, and all of them showed the absence of amino - NH_2 - grouping.

A check experiment with atoxyl was also performed as above. The reaction definitely revealed the presence of NH_2 grouping as shown by the development of the diazo colour.

Further, it was also proved that the above compounds do contain the - NH - imino group. This was proved by the experiments mentioned below :-

A small quantity of the compound was dissolved in dilute hydrochloric acid and sodium nitrite solution (10 %) was added. Yellow coloured liquid was obtained which was treated as follows :

A few crystals of phenol were dissolved in strong sulphuric acid (2.0 c.c.) and a few drops of the above yellow liquid were added ; a blue colour was obtained on warming, which changed to red on dilution with water. Similarly all the compounds were treated as above, and in all cases red colour was observed. This reaction for nitroso compounds definitely reveals the presence of the - NH - grouping in the compounds obtained by the interaction of

atoxyl with the halogen derivatives of acetoacet arylamides and of cyanacet arylamides.

Various methods have been adopted for the estimation of arsenic present in organo arsenicals (21 to 27).

The most convenient method followed, here, was the modification of the method given by St. Warunis (27). In this method, 0.2 to 0.4 gm. of finely powdered compound was carefully fused with a mixture of 5 to 7 gms. of finely powdered anhydrous sodium carbonate and equal amount of sodium peroxide in a nickel crucible for two hours. The melt was, then, dissolved in hot water and the solution carefully acidified with hydrochloric acid. After filtering the solution was neutralised with ammonia and arsenic precipitated as magnesium ammonium arsenate by means of magnesia mixture and ammonia, which after filtration was heated strongly for 2 hours and finally weighed as magnesium pyroarsenate - $Mg_2As_2O_7$.

The mono halogen derivatives of acetoacet arylamides as well as those of cyanacet arylamides, required for the preparation of p-arsonoanilino derivatives, have been prepared by the methods given below :-

Bromo derivatives of acetoacet arylamides :-

Acetoacet arylamide (0.01 M) was dissolved in 10 - 15 ml. of glacial acetic acid in presence of a trace of iodine as catalyst, to which 10 % solution of bromine in acetic acid (16 ml ; 0.01 M) was added with continuous stirring. The flask was, then, kept over-night at room temperature, and the reaction mixture, on pouring into cold

water, gave a white prqduct, which was filtered and crystallised from benzene.

$CH_3COCH_2CONHR + Br_2 \longrightarrow CH_3COCHBrCONHR + HBr$

(Where R is phenyl,tolyl,xylyl and naphthyl groups)

In a similar way using a trace of iodine as catalyst other bromo derivatives of acetoacet arylamides (28) have been prepared in 70-75 % yield.

Chloro derivatives of acetoacet arylamides :

Acetoacet arylamide (0.01 M) was dissolved in 10-15 ml. of glacial acetic acid in presence of a trace of iodine as catalyst ; to it sulphuryl chloride (0.01 M) in cold was added. The reaction mixture was kept for 3 hours at room temperature and, on pouring into cold water, gave a white product, which was filtered and crystallised from alcohol. In some cases a hazy colloidal solution was obtained which when extracted with petroleum ether gave a white product.

$CH_3CO.CH_2.CONHR + SO_2Cl_2 \longrightarrow CH_3COCHCl.CONHR + SO_2 + HCl$

(Where R is phenyl,tolyl,xylyl and naphthyl groups)

Similarly, using a trace of iodine as catalyst in glacial acetic acid, the required number of mono-chloro derivatives have been prepared. It may be pointed out that Naik et al. (29) prepared a few mono-chloro acetoacet arylamides by means of sulphuryl chloride in dry ether, but the method described above, furnished better yields.

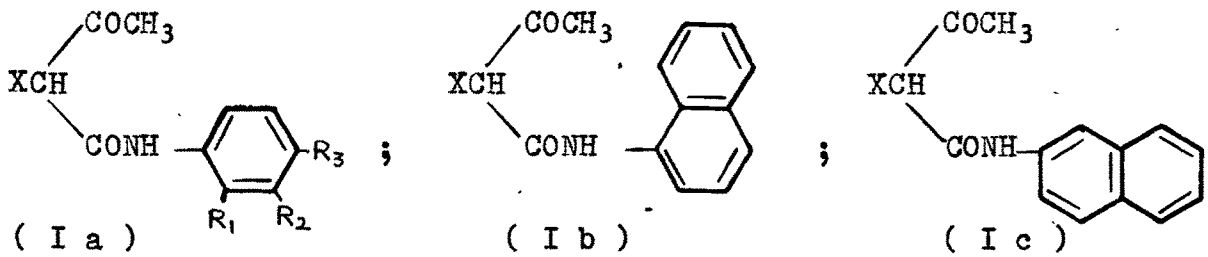
Iodo derivatives of acetoacet and cyanacet arylamide

The mono iodo derivatives of acetoacet arylamides and cyanacet arylamides have been prepared by the method of Avasare et al. (30).

Bromo derivatives of cyanacet arylamide

The mono bromo derivatives of cyanacet arylamide have been prepared by the method of Desai M.N. (31).

Accordingly, the following mono halogen derivatives of acetoacet arylamides have been prepared :



(a) Mono halogen derivatives of acetoacet arylamides

* 1. Mono bromo acetoacet-p-toluidide

(Ia, X=Br ; R_1=R_2=H ; R_3=CH_3)

* 2. Mono bromo acetoacet-o-toluidide

(Ia, X=Br ; R_2=R_3=H ; R_1=CH_3)

* 3. Mono bromo acetoacet-p-chloroanilide

(Ia, X=Br ; R_1=R_2=H ; R_3=Cl)

* 4. Monobromo acetoacet-p-phenitidide

(Ia, X=Br ; R_1=R_2=H ; R_3=OC_2H_5)

* 5. Mono bromo acetoacet-1:2:4-xylidide

(Ia, X=Br ; R_2=H ; R_1=R_3=CH_3)

* 6. Mono bromo acetoacet-1:3:4-xylidide

(Ia, X=Br ; R_1=H ; R_2=R_3=CH_3)

7. Mono bromo acetoacet anilide

(Ia, X=Br ; R_1=R_2=R_3=H)

8. Mono chloro acetoacet anilide

(Ia, X=Cl ; R_1=R_2=R_3=H)

* 9. Mono chloro acetoacet-p-toluidide

(Ia, X=Cl ; R_1=R_2=H ; R_3=CH_3)

10. Mono chloro acetoacet-1:3:4-xylidide

(Ia, X=Cl ; R_1=H ; R_2=R_3=CH_3)

11. Mono chloro acetoacet-α-naphthylamide

(Ib, X=Cl)

* 12. Mono chloro acetoacet-β-naphthylamide

(Ic, X=Cl)

13. Mono iodo acetoacet anilide

(Ia, X=I ; R_1=R_2=R_3=H)

14. Mono iodo acetoacet-o-toluidide

(Ia, X=I ; R_2=R_3=H ; R_1=CH_3)

15. Mono iodo acetoacet-p-toluidide

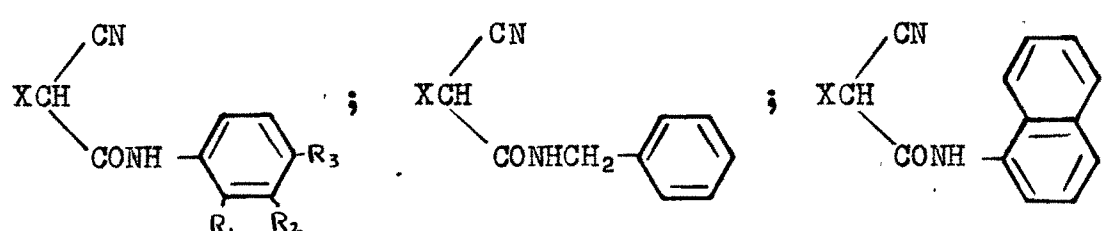
(Ia, X=I ; R_1=R_2=H ; R_3=CH_3)

16. Mono iodo acetoacet-1:3:4-xylidide

(Ia, X=I ; R_1=H ; R_2=R_3=CH_3)

N.B. : The compounds marked with asterisks (*) have been newly prepared.

Similarly, the following mono bromo and mono iodo derivatives of cyanacet arylamides have been prepared :



(II a) (II b) (II c)

(b) Mono bromo and mono iodo derivatives of cyanacetarylamides :

1. Mono bromo cyanacet-o-toluidide
   (IIa, X=Br ; $R_2=R_3=H$; $R_1=CH_3$)
2. Mono bromo cyanacet-p-toluidide
   (IIa, X=Br ; $R_1=R_2=H$; $R_3=CH_3$)
3. Mono bromo cyanacet-benzylamide
   (IIb, X=Br)
4. Mono bromo cyanacet-o-anisidide
   (IIa, X=Br ; $R_2=R_3=H$; $R_1=OCH_3$)
5. Mono bromo cyanacet-p-phenitidide
   (IIa, X=Br ; $R_1=R_2=H$; $R_3=OC_2H_5$)
6. Mono bromo cyanacet-1:3:4-xylidide
   (IIa, X=Br ; $R_1=H$; $R_2=R_3=CH_3$)
7. Mono iodo cyanacetanilide
   (IIa, X=I ; $R_1=R_2=R_3=H$)
8. Mono iodo cyanacet-m-toluidide
   (IIa, X=I ; $R_1=R_3=H$; $R_2=CH_3$)
9. Mono iodo cyanacet-p-toluidide
   (IIa, X=I ; $R_1=R_2=H$; $R_3=CH_3$)
10. Mono iodo cyanacet-1:3:4-xylidide
    (IIa, X=I ; $R_1=H$; $R_2=R_3=CH_3$)
11. Mono iodo cyanacet-α-naphthylamide
    (IIc, X=I)

EXPERIMENTAL

Preparation of mono bromo acetoacet arylamides.

Monobromo acetoacet-p-toluidide

Acetoacet-p-toluidide (1.91 g.) dissolved in 10-15 ml. of glacial acetic acid in presence of a trace of iodine as catalyst, to which 10 % solution of bromine in acetic acid (16 ml.) was slowly added with continuous stirring. The reaction mixture was kept over-night at room temperature and, on dilution, with excess of cold water, gave a white product which was filtered and crystallised from benzene in white shining needles. M.P. 149°C. Yield 1.25 g.

Analysis :

16.0 mg. of the substance gave 11.20 mg. of silver bromide.

Found : Br = 29.79 %.

$C_{11}H_{12}O_2NBr$ requires : Br = 29.67 %.

Monobromo acetoacet-o-toluidide

Acetoacet-o-toluidide (1.91 g.) and bromine in acetic acid (1.6 g.) were treated as above. and the bromo derivative was crystallised from benzene in white needles. M.P. 90°C. Yield 0.95 g.

Analysis :

19.8 mg. of the substance gave 14.16 mg. of silver bromide.

Found : Br = 30.04 %.

$C_{11}H_{12}O_2NBr$ requires : Br = 29.67 %.

Monobromo acetoacet-p-chloroanilide

Acetoacet-p-chloroanilide (2.11 g.) and bromine in acetic acid (1.6 g.) were treated as before, and the bromoderivative was crystallised from benzene in white needles. M.P. 145°C. Yield 1.15 g.

Analysis :

6.134 mg. of the substance gave 0.297 ml. of nitrogen at 29°C and 750 mm. pressure.

Found : N = 5.20 %.

$C_{10}H_9O_2NClBr$ requires : N = 4.82 %.

Monobromo acetoacet-p-phenitidide

Acetoacet-p-phenitidide (2.21 g.) and bromine in acetic acid (1.6 g.) were treated as before, and the product was crystallised from benzene in white needles. M.P. 149°C. Yield 1.65 g.

Analysis :

16.38 mg. of the substance gave 10.32 mg. of silver bromide.

Found : Br = 26.81 %.

$C_{12}H_{14}O_3NBr$ requires : Br = 26.66 %.

Monobromo acetoacet-1:2:4-xylidide

Acetoacet-1:2:4-xylidide (2.05 g.) and bromine in acetic acid (1.6 g.) were treated as above, and the bromo derivative was crystallised from benzene in white needles. M.P. 128°C. Yield 1.3 g.

Analysis :

6.402 mg. of the substance gave 4.222 mg. of silver bromide.

Found : Br = 28.06 %.

$C_{12}H_{14}O_2NBr$ requires : Br = 28.16 %.

Monobromo acetoacet-1:3:4-xylidide

Acetoacet-1:3:4-xylidide (2.05 g.) and bromine in acetic acid (1.6 g.) were treated as above and the product was crystallised from benzene in shining needles, M.P. 126°C. Yield 1.4 g.

Analysis :

10.750 mg. of the substance gave 7.102 mg. of silver bromide.

Found : Br = 28.11 %.

$C_{12}H_{14}O_2NBr$ requires : Br = 28.16 %.

Preparation of mono chloro acetoacet arylamides.

Mono chloro acetoacet-p-toluidide

Acetoacet-p-toluidide (1.91 g.) dissolved in glacial acetic acid (10 ml.) in presence of a trace of iodine as catalyst, to which sulphuryl chloride (1.35 g.) was added in cold. The reaction mixture was kept for three hours at room temperature. On pouring into cold water it gave a white product, which was filtered and crystallised from alcohol in white shining needles. M.P. 86°C. Yield 1.1 g.

Analysis :

6.372 mg. of the substance gave 3.956 mg. of silver chloride.

Found : Cl = 15.36 %.

$C_{11}H_{12}O_2NCl$ requires : Cl = 15.74 %.

Monochloro acetoacet-β-naphthylamide

Acetoacet-β-naphthylamide (2.27 g.) and sulphuryl chloride (1.35 g.) were treated as before and the product was crystallised from alcohol in shining needles. M.P. 93°C. Yield 1.6 g.

Analysis :

8.390 mg. of the substance gave 4.44 mg. of silver chloride.

Found : Cl = 13.10 %.

$C_{14}H_{12}O_2NCl$ requires : Cl = 13.58 %.

Preparation of mono iodo acetoacet and cyanacet-arylamides.

Mono iodo acetoacet anilide

Acetoacet anilide (2.22 g.) dissolved in alcohol (15 ml.) to which iodine (1.27 g.) and iodic acid (0.5 g.) were added with continuous stirring, whereby the iodo derivative was precipitated. It was then filtered and crystallised from alcohol in yellow needles. M.P. 124°C.

Mono iodo cyanacet anilide

Cyanacet anilide (2.0 g.) dissolved in alcohol (60 ml.) to which iodine (1.27 g.) and iodic acid (0.5 g.) were added with continuous stirring. Thus, the mono iodo derivative was precipitated. It was then filtered and crystallised from alcohol in yellowish needles. M.P. 145°C.

Preparation of mono bromo cyanacet arylamides.

Mono bromo cyanacet-o-toluidide

Cyanacet-o-toluidide (1.7 g.) dissolved in

10-15 ml. of glacial acetic acid to which bromine (1.6 g.) in acetic acid (20 % solution) was added to the hot solution with continuous shaking. The flask was kept over-night. Next day it was transferred to evaporating dish and was allowed to evaporate for 2 to 4 days. The product was washed with benzene and petroleum ether and was crystallised from alcohol. M.P. 189°C.

The other mono halo derivatives of acetoacet arylamides and those of cyanacet arylamides required for the preparation of arsonoanilino derivatives have been prepared by the methods described above.

Preparation of p-arsonoanilino derivatives of acetoacet arylamides.

p-Arsonoanilinoacetoacet anilide

(a) Monochloroacetoacet anilide (2.11 g. ; 0.01 M) dissolved in minimum quantity of ethyl alcohol, to which atoxyl (2.39 g. ; 0.01 M) dissolved in 5 ml. of water was added. The reaction mixture was refluxed on a water-bath for three hours. The mixture, on cooling, gave the crude product, which, after charcoaling, was crystallised from aqueous alcohol in tiny floculent clusters. M.P. 240°C. (decomp.). Yield 1.1 g.

Analysis :

0.100 gm. of the substance gave 0.040 gm. of magnesium pyroarsenate- $Mg_2As_2O_7$.

Found : As = 19.33 %.

$C_{16}H_{17}O_5N_2As$ requires : As = 19.12 %.

(b) Monobromoacetoacet anilide (2.56 g. ; 0.01 M) was dissolved in minimum quantity of ethyl alcohol to which atoxyl (2.39 g. ; 0.01 M) dissolved in 5 ml. of water was added. The reaction mixture was refluxed on a water-bath for three hours. The mixture, on cooling, gave the crude product, which, after charcoaling, was crystallised from aqueous alcohol in tiny clusters. M.P. 240°C (decomp.). Yield 1.2 g.

(c) Similarly, monoiodo acetoacetanilide (3.03 g.; 0.01 M) dissolved in minimum quantity of ethyl alcohol, to which atoxyl (2.39 g. ; 0.01 M) dissolved in 5 ml. of water was added. The reaction mixture was refluxed as above for half an hour and the product, after charcoaling, was crystallised from aqueous alcohol in tiny crystals. M.P. 240°C (decomp.). Yield 1.1 g.

p-Arsonoanilino acetoacet anilide obtained, by each of the above mentioned three methods, was found to be identical by comparing their melting points.

p-Arsonoanilinoacetoacet-p-chloroanilide

Monobromoacetoacet-p-chloroanilide (2.9 g.) was dissolved in minimum quantity of ethyl alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as before and the product after charcoaling was crystallised from aqueous alcohol in tiny clusters. M.P. 212°C (decomp.). Yield 1.4 g.

Analysis :

0.152 g. of the substance gave 0.0546 g. of magnesium pyro-arsenate - $Mg_2As_2O_7$.

Found : As = 17.34 %.

$C_{16}H_{16}O_5N_2ClAs$ requires : As = 17.99 %.

p-Arsonoanilinoacetoacet-o-toluidide

(a) Monobromoacetoacet-o-toluidide (2.70 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as before and the product was crystallised from aqueous alcohol in shining clusters. M.P. 226°C (decomp.). Yield 1.2 g.

Analysis :

0.1984 g. of the substance gave 0.0780 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

7.344 mg. of the same substance gave 0.475 ml. of nitrogen at 29°C and 750 mm.pressure.

Found : As = 18.98 % ; N = 7.21 %.

$C_{17}H_{19}O_5N_2As$ requires : As = 18.45 % ; N = 6.90 %.

(b) Monoiodoacetoacet-o-toluidide (3.17 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture, after refluxing for half an hour, was treated as above. The prdduct was crystallised from aqueous alcohol in tiny clusters. M.P. 226°C (decomp.). Yield 1.25 g.

p-Arsonoanilino acetoacet-o-toluidide, obtained by each of the above mentioned two methods, was found to be identical by comparing their melting points.

p-Arsonoanilinoacetoacet-p-toluidide

(a) Monochloroacetoacet-p-toluidide (2.25 g.) was dissolved in ethyl alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was refluxed for three hours and treated as above. The product was crystallised from aqueous alcohol in tiny clusters. M.P. 230°C (decomp.). Yield 1.3 g.

Analysis :

0.100 g. of the substance gave 0.0394 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

7.766 mg. of the same substance gave 0.494 c.c. of nitrogen at 33°C and 745 mm. pressure.

Found : As = 18.87 % ; N = 6.96 %.

$C_{17}H_{19}O_5N_2As$ requires : As = 18.45 % ; N = 6.90 %.

(b) Monobromoacetoacet-p-toluidide (2.7 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was refluxed and treated as above. The product was crystallised from aqueous alcohol in tiny clusters. M.P. 230°C (decomp.). Yield 1.2 g.

(c) Monoiodoacetoacet-p-toluidide (3.17 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was refluxed for half an hour and treated as above. The product was crystallised from aqueous alcohol in shining clusters. M.P. 230°C (decomp.). Yield 1.3 g.

p-Arsonoanilinoacetoacet-p-toluidide, obtained by each of the above mentioned three methods, was found to be identical by comparing their melting points.

p-Arsonoanilino acetoacet-1:2:4-xylidide

Monobromoacetoacet-1:2:4-xylidide (2.84 g.) was dissolved in ethyl alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was refluxed for three hours and was treated as above. The product was crystallised from aqueous alcohol in tiny clusters. M.P. 218°C (decomp.). Yield 1.25 g.

Analysis :

0.174 g. of the substance gave 0.0616 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

Found : As = 17.19 %.

$C_{18}H_{21}O_5N_2As$ requires : As = 17.84 %.

p-Arsonoanilino acetoacet-1:3:4-xylidide

(a) Monochloro acetoacet-1:3:4-xylidide (2.39 g.) was dissolved in ethyl alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as above ; and the product was crystallised from aqueous alcohol in shining tiny clusters. M.P. 226°C (decomp.). Yield 1.0 g.

Analysis :

0.1824 g. of the substance gave 0.0652 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

6.970 mg. of the same substance gave 0.425 c.c. of nitrogen at 39°C and 752 mm. pressure.

Found : As = 17.25 % ; N = 6.6 %.

$C_{18}H_{21}O_5N_2As$ requires : As = 17.84 % ; N = 6.7 %.

(b) Monobromo acetoacet-1:3:4-xylidide (2.84 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as before and the product was crystallised from aqueous alcohol in tiny crystals. M.P. 226°C (decomp.). Yield 0.9 g.

(c) Monoiodo acetoacet-1:3:4-xylidide (3.17 g.) was dissolved in alcohol to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was refluxed for half an hour and treated as above. The product was crystallised from aqueous alcohol in tiny clusters. M.P. 226°C (decomp.). Yield 1.1 g.

p-Arsonoanilino acetoacet-1:3:4-xylidide, obtained by each of the above mentioned three methods, was found to be identical by comparing their melting points.

p-Arsonoanilino acetoacet-p-phenitidide

Monobromo acetoacet-p-phenitidide (3.0 g.) was dissolved in alcohol to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as before and the product was crystallised from aqueous alcohol in tiny clusters. M.P. 198°C (decomp.). Yield 1.2 g.

Analysis :

0.100 g. of the substance gave 0.035 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

Found : As = 16.93 %.

$C_{18}H_{21}O_6N_2As$ requires : As = 17.19 %.

p-Arsonoanilino acetoacet-α-naphthylamide

Monochloro acetoacet-α-naphthylamide (2.61 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as before ; and the product was crystallised from aqueous alcohol in tiny clusters.M.P. 252°C. Yield 1.3 g.

Analysis :

0.164 g. of the substance gave 0.0592 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

8.532 mg. of the same substance gave 0.465 c.c. of nitrogen at 35°C and 746 mm. pressure.

Found : As = 17.47 % ; N = 5.93 %.

$C_{20}H_{19}O_5N_2As$ requires : As = 16.91 % ; N = 6.32 %.

p-Arsonoanilino acetoacet-β-naphthylamide

Monochloro acetoacet-β-naphthylamide (2.61 g.) was dissolved in ethyl alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as above ; and the product was crystallised from aqueous alcohol in tiny clusters. M.P. 268°C (decomp.). Yield 1.2 g.

Analysis :

0.142 g. of the substance gave 0.048 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

Found : As = 16.32 %.

$C_{20}H_{19}O_5N_2As$ requires : As = 16.91 % .

Preparation of p-arsonoanilino derivatives of cyanacet arylamides.

p-Arsonoanilino cyanacet anilide

Monoiodo cyanacet anilide (2.86 g. ; 0.01 M) was dissolved in minimum quantity of ethyl alcohol, to which atoxyl (2.39 g. ; 0.01 M) dissolved in 5 ml. of water was added. The reaction mixture was refluxed for half an hour and then treated as above. The product was crystallised from aqueous alcohol in tiny clusters. M.P. 225°C (decomp.). Yield 1.1 g.

Analysis :

0.1464 g. of the substance gave 0.0594 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

Found : As = 19.58 %.

$C_{15}H_{14}O_4N_3As$ requires : As = 20.00 %.

p-Arsonoanilino cyanacet-o-toluidide

Monobromo cyanacet-o-toluidide (2.53 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was refluxed for three hours and treated as before. The product was crystallised from aqueous alcohol in tiny clusters. M.P. 212°C(decomp.). Yield 0.9 g.

Analysis :

0.1782 g. of the substance gave 0.072 g. of magnesium pyroarsenate - $Mg_2As_2O_7$,

Found : As = 19.50 %.

$C_{16}H_{16}O_4N_3As$ requires : As = 19.29 %.

p-Arsonoanilino cyanacet-m-toluidide

Monoiodo cyanacet-m-toluidide (3.0 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as before. The product was crystallised from aqueous alcohol in shining clusters. M.P. 197°C (decomp.). Yield 1.0 g.

Analysis :

0.1384 g. of the substance gave 0.0570 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

Found : As = 20.02 %.

$C_{16}H_{16}O_4N_3As$ requires : As = 19.29 %.

p-Arsonoanilino cyanacet-p-toluidide

(a) Monobromo cyanacet-p-toluidide (2.53 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as above ; and the product was crystallised from aqueous alcohol in shining clusters. M.P. 255°C (decomp.). Yield 1.1 g.

Analysis :

0.1696 g. of the substance gave 0.0656 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

7.522 mg. of the same substance gave 0.752 c.c. of nitrogen at 34°C and 745 mm. pressure.

Found : As = 18.66 % ; N = 10.9 %.

$C_{16}H_{16}O_4N_3As$ requires : As = 19.29 % ; N = 10.8 %.

(b) Monoiodo cyanacet-p-toluidide (3.0 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as above ; and the product was crystallised from aqueous alcohol in shining crystals. M.P. 255°C (decomp.). Yield 1.2 g.

p-Arsonoanilino cyanacet-p-toluidide, obtained by each of the above mentioned two methods, was found to be identical by comparing their melting points.

p-Arsonoanilino cyanacet benzylamide

Monobromo cyanacet benzylamide (2.53 g.) was dissolved in alcohol, to which atoxyl (2.39 g.)dissolved in 5 ml. of water was added. The reaction mixture was refluxed and treated as above. The product was crystallised from aqueous alcohol in shining clusters. M.P. 208°C(decomp.). Yield 1.15 g.

Analysis :

0.174 g. of the substance gave 0.0722 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

Found : As = 19.94 %.

$C_{16}H_{16}O_4N_3As$ requires : As = 19.29 %.

p-Arsonoanilino cyanacet-o-anisidide

Monobromo cyanacet-o-anisidide (2.69 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as above. The product was crystallised from aqueous alcohol in tiny clusters. M.P. 232°C (decomp.). Yield 1.35 g.

Analysis :

0.202 g. of the substance gave 0.0808 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

Found : As = 19.21 %.

$C_{16}H_{16}O_5N_3As$ requires : As = 18.52 %.

p-Arsonoanilino cyanacet-p-phenitidide

Monobromo cyanacet-p-phenitidide (2.83 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as above. The product was crystallised from aqueous alcohol in tiny clusters. M.P. 259°C (decomp.). Yield 1.2 g.

Analysis :

0.122 g. of the substance gave 0.044 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

Found : As = 17.41 %.

$C_{17}H_{18}O_5N_3As$ requires : As = 17.90 %.

p-Arsonoanilino cyanacet-1:3:4-xylidide

(a)Monobromo cyanacet-1:3:4-xylidide (2.67 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as above. The product was crystallised from aqueous alcohol in shining clusters. M.P. 262°C (decomp.). Yield 1.1 g.

Analysis :

0.100 g. of the substance gave 0.038 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

5.060 mg. of the same substance gave 0.475 c.c. of nitrogen at 32°C and 747 mm. pressure.

Found : As = 18.38 % /; N = 10.33 %.

$C_{17}H_{18}O_4N_3As$ requires : As = 18.61 % ; N = 10.42 %.

(b) Monoiodo cyanacet-1:3:4-xylidide (3.1 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in water was added. The reaction mixture was treated as above. The product was crystallised from aqueous alcohol in tiny clusters. M.P. 262°C (decomp.). Yield 1.2 g.

p-Arsonoanilino cyanacet-1:3:4-xylidide, obtained by each of the above mentioned two methods, was found to be identical by comparing their melting points.

p-Arsonoanilino cyanacet-α-naphthalmide

Monoiodo cyanacet-α-naphthylamide (3.36 g.) was dissolved in alcohol, to which atoxyl (2.39 g.) dissolved in 5 ml. of water was added. The reaction mixture was treated as above. The product was crystallised from aqueous alcohol in tiny clusters. M.P. 282°C (decomp.). Yield 1.4 g.

Analysis :

0.198 g. of the substance gave 0.0714 g. of magnesium pyroarsenate - $Mg_2As_2O_7$.

Found : As = 17.42 %.

$C_{19}H_{16}O_4N_3As$ requires : As = 17.65 %.

Table 4

Mono halo acetoacet arylamides

S.No.	Compound	Molecular Formula	M.P. °C	Yield %	Halogen Found %	Halogen regd. %	Nitrogen Found %	Nitrogen regd. %
* 1.	Monobromo acetoacet-p-toluidide	$C_{11}H_{12}O_2NBr$	149	65.8	29.79	29.67	-	-
* 2.	Monobromo acetoacet-o-toluidide	$C_{11}H_{12}O_2NBr$	90	50.0	30.04	29.67	-	-
* 3.	Monobromo acetoacet-p-chloroanilide	$C_{10}H_9O_2NClBr$	145	61.5	-	-	5.20	4.82
* 4.	Monobromo acetoacet-p-phenitidide	$C_{12}H_{14}O_3NBr$	149	75.0	26.81	26.66	-	-
* 5.	Monobromo acetoacet-1:2:4-xylidide	$C_{12}H_{14}O_2NBr$	128	66.0	28.06	28.16	-	-
* 6.	Monobromo acetoacet-1:3:4-xylidide	$C_{12}H_{14}O_2NBr$	126	70.0	28.11	28.16	-	-
7.	Monobromo acetoacet anilide	$C_{10}H_{10}O_2NBr$	136	-	-	-	-	-
8.	Monochloro acetoacet anilide	$C_{10}H_{10}O_2NCl$	138	-	-	-	-	-

Table 4 (Contd.)

S.No.	Compound	Molecular Formula	M.P. °C	Yield %	Halogen Found %	Halogen reqd. %	Nitrogen Found %	Nitrogen reqd. %
* 9.	Monochloro acetoacet-p-toluidide	$C_{11}H_{12}O_2NCl$	86	57.6	15.36	15.74	-	-
10.	Monochloro acetoacet-1:3:4-xylidide	$C_{12}H_{14}O_2NCl$	114	-	-	-	-	-
11.	Monochloro acetoacet-α-naphthylamide	$C_{14}H_{12}O_2NCl$	135	-	-	-	-	-
* 12.	Monochloro acetoacet-β-naphthylamide	$C_{14}H_{12}O_2NCl$	93	70.5	13.10	13.58	-	-
13.	Monoiodo acetoacet anilide	$C_{10}H_{10}O_2NI$	124	-	-	-	-	-
14.	Mono-iodo acetoacet-o-toluidide	$C_{11}H_{12}O_2NI$	128	-	-	-	-	-
15.	Monoiodo acetoacet-p-toluidide	$C_{11}H_{12}O_2NI$	121	-	-	-	-	-
16.	Monoiodo acetoacet-1:3:4-xylidide	$C_{12}H_{14}O_2NI$	131	-	-	-	-	-

Table 5

Mono halo cyanacet arylamides

S.No.	Compound	Molecular formula	M.P. ^{o}C
1.	Monobromo cyanacet-o-toluidide	$C_{10}H_9ON_2Br$	189
2.	Monobromo cyanacet-p-toluidide	$C_{10}H_9ON_2Br$	186
3.	Monobromo cyanacet-benzylamide	$C_{10}H_9ON_2Br$	150
4.	Monobromo cyanacet-o-anisidide	$C_{10}H_9O_2N_2Br$	163
5.	Monobromo cyanacet-p-phenitidide	$C_{11}H_{11}O_2N_2Br$	187
6.	Monobromo cyanacet-1:3:4-xylidide	$C_{11}H_{11}ON_2Br$	171
7.	Monoiodo cyanacet anilide	$C_9H_7ON_2I$	145
8.	Monoiodo cyanacet-m-toluidide	$C_{10}H_9ON_2I$	163
9.	Monoiodo cyanacet-p-toluidide	$C_{10}H_9ON_2I$	166
10.	Monoiodo cyanacet-1:3:4-xylidide	$C_{11}H_{11}ON_2I$	161
11.	Monoiodo cyanacet-α-naphthylamide	$C_{13}H_9ON_2I$	202

Table 6

p-Arsonoanilino acetoacet arylamides

S.No.	Compound	Molecular formula	M.P. °C	Yield %	Arsenic Found %	Arsenic reqd. %	Nitrogen Found %	Nitrogen reqd. %
1.	p-Arsonoanilino acetoacet anilide	$C_{16}H_{17}O_5N_2As$	240	28.13	19.33	19.12	-	-
2.	p-Arsonoanilino acetoacet-p-chloroanilide	$C_{16}H_{16}O_5N_2ClAs$	212	33.62	17.34	17.99	-	-
3.	p-Arsonoanilino acetoacet-o-toluidide	$C_{17}H_{19}O_5N_2As$	226	29.63	18.98	18.45	7.21	6.90
4.	p-Arsonoanilino acetoacet-p-toluidide	$C_{17}H_{19}O_5N_2As$	230	32.09	18.87	18.45	6.96	6.90
5.	p-Arsonoanilino acetoacet-1:2:4-xylidide	$C_{18}H_{21}O_5N_2As$	218	29.84	17.19	17.84	-	-
6.	p-Arsonoanilino acetoacet-1:3:4-xylidide	$C_{18}H_{21}O_5N_2As$	226	23.86	17.25	17.84	6.60	6.67
7.	p-Arsonoanilino acetoacet-p-phenitidide	$C_{18}H_{21}O_6N_2As$	198	27.58	16.93	17.19	-	-
8.	p-Arsonoanilino acetoacet-α-naphthylamide	$C_{20}H_{19}O_5N_2As$	252	29.41	17.47	16.91	5.93	6.32
9.	p-Arsonoanilino acetoacet-β-naphthylamide	$C_{20}H_{19}O_5N_2As$	268	27.15	16.32	16.91	-	-

Table 7

p-Arsonoanilino cyanacet arylamides

S.No.	Compound	Molecular formula	M.P. °C	Yield %	Arsenic Found %	Arsenic reqd. %	Nitrogen Found %	Nitrogen reqd. %
1.	p-Arsonoanilino cyanacet anilide	$C_{15}H_{14}O_4N_3As$	225	29.34	19.58	20.00	-	-
2.	p-Arsonoanilino cyanacet-o-toluidide	$C_{16}H_{16}O_4N_3As$	212	23.14	19.50	19.29	-	-
3.	p-Arsonoanilino cyanacet-m-toluidide	$C_{16}H_{16}O_4N_3As$	197	25.71	20.02	19.29	-	-
4.	p-Arsonoanilino cyanacet-p-toluidide	$C_{16}H_{16}O_4N_3As$	255	28.28	18.66	19.29	10.90	10.80
5.	p-Arsonoanilino cyanacet-benzylamide	$C_{16}H_{16}O_4N_3As$	208	29.56	19.94	19.29	-	-
6.	p-Arsonoanilino cyanacet-o-anisidide	$C_{16}H_{16}O_5N_3As$	232	34.10	19.21	18.52	-	-
7.	p-Arsonoanilino cyanacet-p-phenitidide	$C_{17}H_{18}O_5N_3As$	259	28.64	17.41	17.90	-	-
8.	p-Arsonoanilino cyanacet-1:3:4-xylidide	$C_{17}H_{18}O_4N_3As$	262	32.25	18.38	18.61	10.33	10.42
9.	p-Arsonoanilino cyanacet-α-naphthylamide	$C_{19}H_{16}O_4N_3As$	282	32.94	17.42	17.65	-	-

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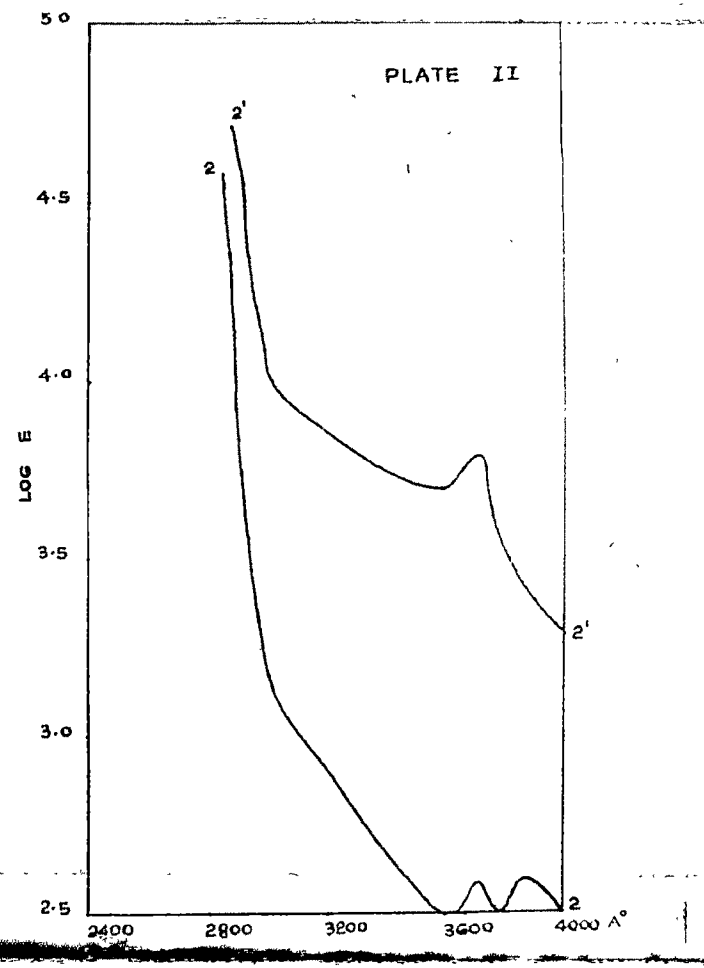
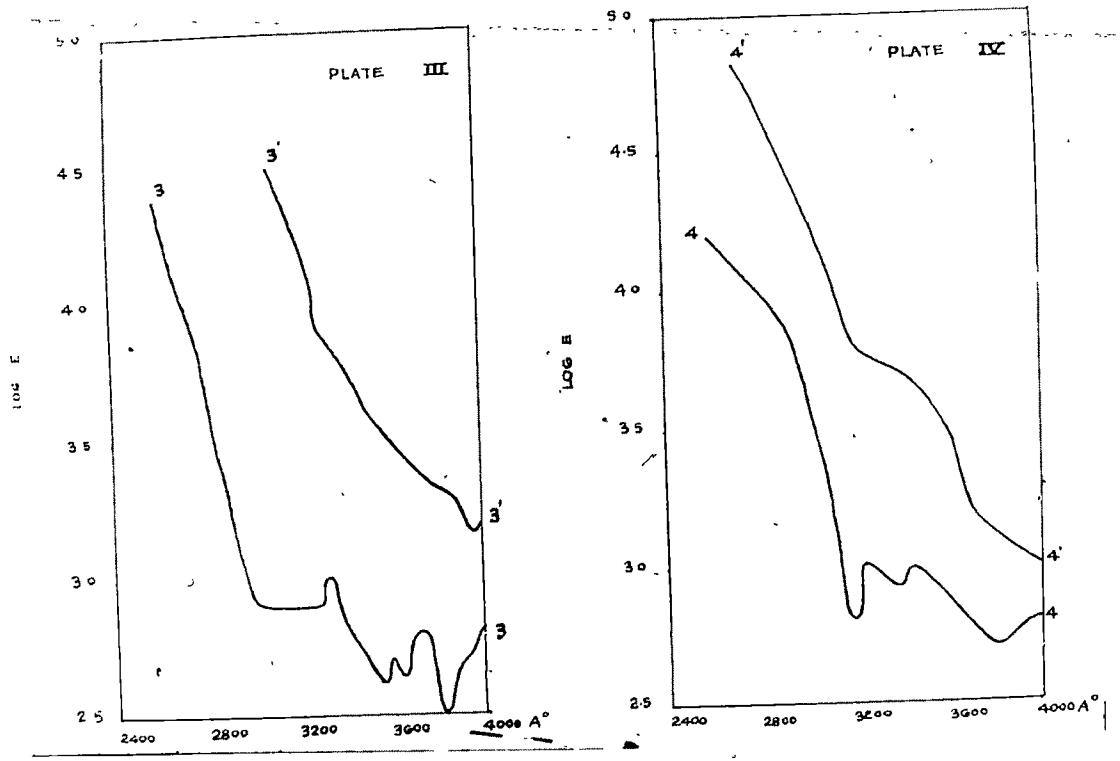
(1) Cyanacet anilide and (1') its methylene bis-derivative.

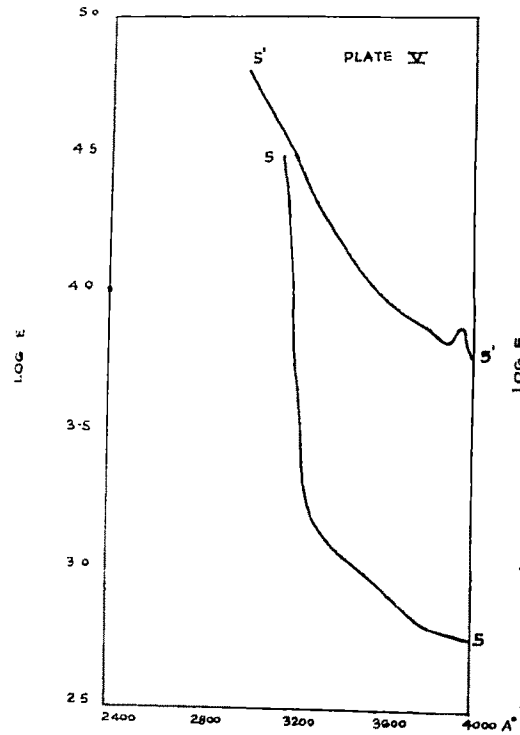


(2) Cyanacet-p-chloroanilide and (2') its methylene bis-derivative.

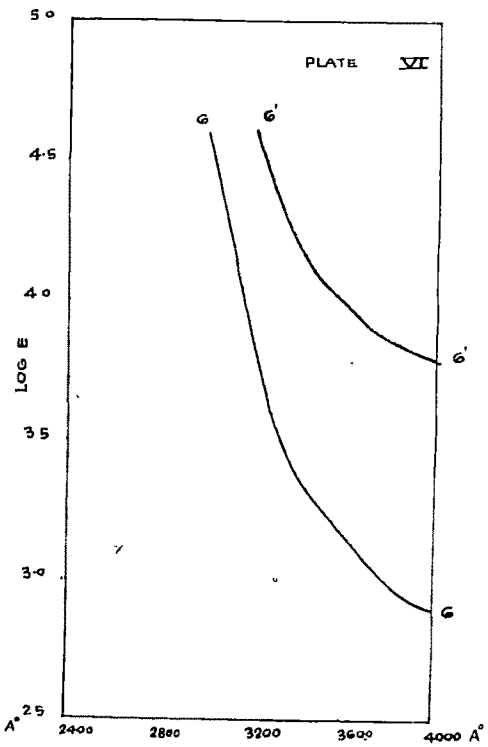


(3) Cyanacet-p-toluidide and (3') its methylene bis-derivative.

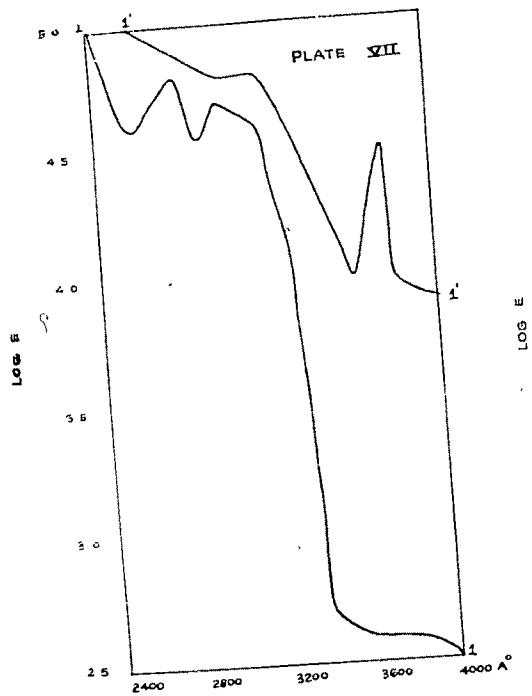
(4) Cyanacet-1.3.4-xylidide and (4') its methylene bis-derivative.



(5) Cyanacet-α-naphthylamide and (5') its methylene bis-derivative.



(6) Cyanacet-β-naphthylamide and (6') its methylene bis-derivative.



(1) 2,4-Dihydroxyquinoline and (1') its methylene bis-derivative.

(2) 6-Methyl-2,4-dihydroxyquinoline and (2') its methylene bis-derivative.