# **449.** *Compounds of Diarylcyanoarsine Type.*

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A considerable number of diarylarsonous acids have been made by the use of the Bart reaction, and converted by reduction in the presence of hydrochloric acid into the corresponding diarylchloroarsines. From these and other diarylchloroarsines obtained by alternative methods many diarylcyanoarsines have been prepared.

During investigations undertaken in order to obtain a series of compounds of diarylcyanoarsine type, AsRR'·CN, the reaction of Bart (D.R.-P. 250,264; *Chem. Zentr.*, 1912, ii, 882; *Annalen*, 1922, **429**, 55) has been applied to the preparation of a number of diarylarsonous acids, AsRR'O·OH.* It is of interest that although phenyl- and the three tolyl-arsenious oxides, R·AsO, readily coupled as sodium salts with a variety of diazotised amines, *o*- and *p*-chlorophenylarsenious oxides could not be made to undergo the reaction with aniline or *o*-chloroaniline, the only products isolated being the corresponding chlorophenylarsonic acids, formed by oxidation of the oxides.

Many of the diarylchloroarsines, AsRR'Cl, required for conversion into the cyanoarsines were obtained from these diarylarsonous acids by reduction with sulphur dioxide in the presence of hydrochloric acid, but a few of the symmetrical ones were prepared by heating the appropriate aryldichloroarsine, $AsRCl_2$, with three molecular proportions of the corresponding arylarsenious oxide (the Pope–Turner process). The method of Steinkopf (*Annalen*, 1917, **413**, 310), using 2-thienylmercury chloride and arsenic trichloride, has been modified to give more satisfactory yields of di-2-thienylchloroarsine, and *phenyl-2-thienylchloroarsine* has been prepared, first from 2-thienylmercury chloride and phenyldichloroarsine, and secondly from phenylmercury chloride and 2-thienyldichloroarsine. The diarylcyanoarsines were obtained from the chloroarsines by the action of sodium cyanide.

p-*Phenylenebisdichloroarsine*, $C_6H_4(AsCl_2)_2$, has been prepared by reduction of *p*-phenylenediarsonic acid with sulphur dioxide in the presence of hydrogen chloride.

## Experimental.

### *Diarylarsonous Acids.*

*Di*-m-*tolylarsonous Acid*.—The following procedure is based upon a method developed before 1940 at the Ministry of Supply Research Establishment, Sutton Oak, for the preparation of diphenylarsonous acid. *m*-Toluidine (21·8 g.) in concentrated hydrochloric acid (42·5 c.c.) and water (85 c.c.), was diazotised below 0° by the addition of sodium nitrite (14·7 g.) in water (45 c.c.), and the solution made neutral to Congo-red with concentrated aqueous sodium carbonate. Meanwhile *m*-tolylarsenious oxide (37 g.) was dissolved by warming with aqueous sodium hydroxide (23 c.c. of 36·7%) and water (30 c.c.), and the solution diluted with more water (730 c.c.) and filtered. The diazo-solution was kept below 0° and mechanically stirred while the arsenious oxide solution was added dropwise below the surface during 2 hours, a little nitrobenzene being added occasionally to dispel the froth. Stirring was then continued for a further 2 hours below 0°, after which the mixture was left overnight. Aqueous sodium hydroxide (8 c.c. of 36·7%) was added, the whole stirred for an hour, the tarry material removed by filtration, and the filtrate stirred with charcoal for 20 minutes at room temperature. After being again filtered, the

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* By a recent decision the oxyacids of phosphorus, arsenic, and antimony are now named as in the following examples :

| | | | |
|---|---|---|---|
| $PRO(OH)_2$ | $PR(OH)_2$ | $PR_2O{\cdot}OH$ | $PR_2{\cdot}OH$ |
| Phosphonic | Phosphinic | Phosphonous | Phosphinous |

The compounds AsRR'O·OH, which under I.U.C. Rule 34 would be called arsinic acids, are therefore here called arsonous acids.—Editor.

solution was treated with ice, and acidified (Congo-red) with concentrated hydrochloric acid. The precipitate (8 g.) was crystallised from aqueous alcohol, from which *di*-m-*tolylarsonous acid* separated in colourless needles, m. p. 140—143° (Found : C, 57·7; H, 5·2. $C_{14}H_{15}O_2As$ requires C, 57·9; H, 5·2%).

The following were prepared by a similar process, the starting materials which were used being indicated, where necessary, by giving the amine. The yields were generally between 10% and 30% of the theoretical, but no figures are given because several of the preparations have been made only once, and adjustment of the conditions would no doubt give improved results : *phenyl*-o-*tolylarsonous acid* (from *o*-toluidine), colourless prisms, m. p. 163°, from aqueous alcohol (Found : C, 55·5; H, 4·6. $C_{13}H_{13}O_2As$ requires C, 56·5; H, 4·7%); *phenyl*-m-*tolylarsonous acid* (from *m*-toluidine), colourless prisms, m. p. 117—119°, from aqueous alcohol (Found : C, 54·9; H, 4·6%); *phenyl*-m-4-*xylylarsonous acid* (from *m*-4-xylidine), colourless needles, m. p. 165—167°, from water (Found : C, 58·1; H, 5·4%); *di*-o-*tolylarsonous acid*, colourless prisms, m. p. 197°, from alcohol (Found : C, 57·0; H, 5·0%); o-*tolyl*-m-*tolylarsonous acid* (from *m*-toluidine), colourless plates, m. p. 129—131°, from aqueous alcohol (Found : C, 56·7; H, 5·2%); *o*-tolyl-*p*-tolylarsonous acid (from *o*-toluidine); m-*tolyl*-p-*tolylarsonous acid* (from *m*-toluidine), yellow prisms, m. p. 145—146°, from aqueous alcohol (Found : C, 58·2; H, 5·2%); di-*p*-tolylarsonous acid, m. p. 171° (cf. La Coste, *Annalen*, 1881, **208**, 1; Matsumiya and Nakai, *Chem. Zentr.*, 1926, i, 652; 1927, i, 1302); o-*tolyl*-m-4-*xylylarsonous acid* (from *m*-4-xylidine), colourless needles, m. p. 184—185°, from aqueous alcohol (Found : C, 58·3; H, 5·4. $C_{15}H_{17}O_2As$ requires C, 59·2; H, 5·6%); p-*tolyl*-m-4-*xylylarsonous acid* (from *m*-4-xylidine), colourless needles, m. p. 138—140°, from aqueous alcohol (Found : C, 58·2; H, 5·5%); 2-*chlorodiphenylarsonous acid* (from *o*-chloroaniline), m. p. 184—186° (Found : C, 48·4; H, 3·7. $C_{12}H_{10}O_2ClAs$ requires C, 48·6; H, 3·4%); 4-chlorodiphenylarsonous acid (from *p*-chloroaniline), m. p. 161° (Found : C, 48·0; H, 3·4%) (cf. Mann and Watson, *J.*, 1947, 505); o-*chlorophenyl*-o-*tolylarsonous acid* (from *o*-chloroaniline), colourless prisms, m. p. 218—224°, from aqueous alcohol (Found : C, 50·9; H, 4·2. $C_{13}H_{12}O_2ClAs$ requires C, 50·2; H, 3·9%); p-*chlorophenyl*-o-*tolylarsonous acid* (from *p*-chloroaniline), colourless prisms, m. p. 131—134°, from acetone (Found : C, 49·0; H, 3·5%); o-*chlorophenyl*-p-*tolylarsonous acid* (from *o*-chloroaniline), colourless prisms, m. p. 170—172°, from aqueous alcohol (Found : C, 50·1; H, 4·0%); m-*chlorophenyl*-p-*tolylarsonous acid* (from *m*-chloroaniline), colourless prisms, m. p. 124—125°, from aqueous alcohol (Found : C, 49·8; H, 4·0%); p-*chlorophenyl*-p-*tolylarsonous acid* (from *p*-chloroaniline), colourless needles, m. p. 144°, from aqueous alcohol (Found : C, 50·2; H, 3·9%); p-*nitrophenyl*-p-*tolylarsonous acid* (from *p*-nitroaniline), colourless needles, m. p. 142—144°, from water (Found : C, 48·5; H, 3·9. $C_{13}H_{12}O_4NAs$ requires C, 48·6; H, 3·7%); 3-*formyldiphenylarsonous acid* (from *m*-aminobenzaldehyde), colourless prisms, m. p. 168° (softens at 163°), from water (Found : C, 52·4; H, 4·0. $C_{13}H_{11}O_3As$ requires C, 53·8; H, 3·8%) [its 2 : 4-*dinitrophenylhydrazone* separated from alcohol in yellow prisms, m. p. 270° (decomp.) (Found : N, 12·1. $C_{19}H_{15}O_6N_4As$ requires N, 11·9%)]; 3-*acetyldiphenylarsonous acid* (from *m*-aminoacetophenone), colourless needles, m. p. 146—148°, from aqueous alcohol (Found : C, 55·4; H, 4·4. $C_{14}H_{13}O_3As$ requires C, 55·3; H, 4·3%); 3-*carboxydiphenylarsonous acid* (from *m*-aminobenzoic acid), yellow prisms, m. p. 215° (decomp.), from aqueous alcohol (Found : C, 51·3; H, 3·6. $C_{13}H_{11}O_4As$ requires C, 51·0; H, 3·6%); 4-*carboxydiphenylarsonous acid* (from *p*-aminobenzoic acid), almost colourless needles, m. p. 229—231°, from aqueous alcohol (Found : C, 51·2; H, 3·8%); phenyl-1-naphthylarsonous acid (from α-naphthylamine), m. p. 181—183° (cf. Blicke and Smith, *J. Amer. Chem. Soc.*, 1929, **51**, 3479; Klippel, *Chem. Zentr.*, 1931, i, 1440); *phenyl*-2-*naphthylarsonous acid* (from β-naphthylamine), m.p. 157—159° (Found : C, 58·6; H, 4·3. $C_{16}H_{13}O_2As$ requires C, 61·5; H, 4·2%); p-*tolyl*-1-*naphthylarsonous acid* (from α-naphthylamine), colourless plates, m. p. 198—200°, from aqueous alcohol (Found : C, 62·4; H, 4·8. $C_{17}H_{15}O_2As$ requires C, 62·6; H, 4·6%); p-*tolyl*-2-*naphthylarsonous acid* (from β-naphthylamine), pale pink prisms, m. p. 160—162°, from aqueous alcohol (Found : C, 62·6; H, 4·6%).

m-*Chlorophenyl*-o-*tolylarsonous Acid*.—The following process was based upon conditions developed by Professor A. R. Todd in 1940 for diphenylarsonous acid, and communicated by the Ministry of Supply. A suspension of the hydrochloride of *m*-chloroaniline (25 g. of the base) in concentrated hydrochloric acid (45 c.c.) was cooled to −15° by the addition of ice, and diazotised below 0° by the gradual addition of sodium nitrite (14 g.) during 15 minutes. The solution was then made just neutral to Congo-red with aqueous sodium carbonate. *o*-Tolylarsenious oxide (35·7 g.) was dissolved in 10% sodium hydroxide solution (125 c.c.), and water added to make the volume up to 250 c.c. The diazo- and oxide solutions were added simultaneously below the surface to a solution of Lissapol LS (1 g.) in water (50 c.c.) immersed in an ice-bath and vigorously stirred. The diazo-solution was added slightly in advance of the oxide solution, and during the process, which was completed in about 1½ hours, the temperature was kept at 0°. A few drops of nitrobenzene were added to prevent excessive frothing, and the mixture was kept slightly alkaline to brilliant-yellow paper by addition of sodium carbonate solution as necessary. Sodium carbonate (10 g.) was then added in portions during 1 hour, and stirring continued, still with an ice-bath, until the presence of the diazo-compound could no longer be detected by means of H-acid. The solution was filtered to remove a considerable amount of tarry material, stirred for some time with charcoal, and again filtered. On acidification (to Congo-red) with hydrochloric acid, m-*chlorophenyl*-o-*tolylarsonous acid* (11 g.) was precipitated as a gum, but this crystallised after a few hours. After crystallisation from aqueous alcohol, it was obtained in colourless prisms, m. p. 138° (Found : C, 50·1; H, 3·8%).

The following were prepared by a process similar to the above : o-*nitrophenyl*-o-*tolylarsonous acid* (from *o*-nitroaniline), pale yellow prisms, m. p. 220—221° (with darkening), from alcohol (Found : C, 48·6; H, 3·8%); m-*nitrophenyl*-o-*tolylarsonous acid* (from *m*-nitroaniline), colourless prisms, m. p. 183—186°, from water (Found : C, 48·6; H, 3·9%); p-*nitrophenyl*-o-*tolylarsonous acid* (from *p*-nitroaniline), colourless prisms, m. p. 169—171°, from alcohol (Found : C, 48·6; H, 3·9%).

2-*Acetamidodiphenylarsonous Acid*.—A solution of 2-nitrodiphenylarsonous acid (45 g., prepared by the method of Sakellarios, *Ber.*, 1924, **57**, 1514) and sodium hydroxide (35 g.) in water (450 c.c.) was added in a thin stream to a suspension of ferrous hydroxide prepared by adding sodium hydroxide (110 g. in 400 c.c. of water) to a rapidly stirred solution of ferrous sulphate (255 g.) in water (700 c.c.). After the mixture had been stirred for 3 hours, it was left for a day and then filtered. The filtrate was mechanically stirred and treated gradually with hydrochloric acid (12%) until it became turbid. A few c.c. of dilute acetic acid were then added, and the gummy pink precipitate was filtered off. This process was repeated with further successive small amounts of acetic acid until a crystalline precipitate began to form. The precipitation of 2-aminodiphenylarsonous acid (25 g., m. p. 129—130°; cf. Kalb, *Annalen*, 1921, **423**, 39) was then completed by addition of excess of acetic acid. A mixture of the amino-acid (10 g.), acetic anhydride (20 c.c.), acetic acid (100 c.c.), and concentrated sulphuric acid (0·5 c.c.) was heated on a steam-bath for an hour, and most of the volatile material then removed by distillation under reduced pressure. When water was added and the solution concentrated to small bulk, 2-*acetamidodiphenylarsonous acid* (8 g.) separated. After crystallisation from alcohol (charcoal), it melted at 193—195° (Found : C, 52·1; H, 4·5; N, 4·4. $C_{14}H_{14}O_3NAs$ requires C, 52·7; H, 4·4; N, 4·4%).

### *Diarylchloroarsines.*

2-*Chlorodiphenylchloroarsine*.—2-Chlorodiphenylarsonous acid (15 g.) was suspended in concentrated hydrochloric acid (30 c.c.) at 90° a crystal of potassium iodide was added, and sulphur dioxide was passed through with mechanical stirring for 2 hours. When cold, the oily product was extracted with carbon tetrachloride, and the extract dried ($Na_2SO_4$). After the solvent had been removed by distillation from a water-bath under reduced pressure, 2-*chlorodiphenylchloroarsine* remained as an oil which solidified on being cooled in a freezing mixture. It then melted at 30—35° (Found : hydrolysable Cl, 12·6. $C_{12}H_9Cl_2As$ requires hydrolysable Cl, 11·9%).

The following were similarly prepared from the corresponding derivatives of diphenylarsonous acid : o-*nitrophenyl*-o-*tolylchloroarsine*, yellow prisms, m. p. 93—96°, from petroleum (b. p. 60—80°) (Found : N, 4·4; Cl, 10·7. $C_{13}H_{11}O_2NClAs$ requires N, 4·3; Cl, 11·0%); p-*nitrophenyl*-p-*tolylchloroarsine*, yellow needles, m. p. 94—96°, from methyl alcohol (Found : Cl, 9·2%); 3-*acetyldiphenylchloroarsine*, colourless prisms, m. p. 71—72°, from petroleum (b. p. 60—80°) (Found : Cl, 11·6. $C_{14}H_{12}OClAs$ requires Cl, 11·6%); *diphenylchloroarsine*-3-*carboxylic acid*, colourless prisms, m. p. 134—136°, from benzene (Found : Cl, 10·6. $C_{13}H_{10}O_2ClAs$ requires Cl, 11·5%); *diphenylchloroarsine*-4-*carboxylic acid*, colourless prisms, m. p. 115—117°, from benzene–petroleum (b. p. 60—80°) (Found : Cl, 10·7%); 2-*acetamidodiphenylchloroarsine* (prepared at room temperature), colourless needles, m. p. 162—164°, from benzene (Found : C, 53·3; H, 4·2; Cl, 10·6. $C_{14}H_{13}ONClAs$ requires C, 52·3; H, 4·0; Cl, 11·0%). A number of other derivatives of diphenylchloroarsine were formed by a similar process as intermediates in the preparation of the cyanoarsines described below, but were not characterised.

*Methyl Diphenylchloroarsine*-3-*carboxylate*.—After diphenylchloroarsine-3-carboxylic acid (5 g.) had been refluxed for 10 hours with methyl alcohol (50 c.c.) saturated with hydrogen chloride, the solvent was removed by distillation under reduced pressure until frothing became troublesome. The residue was dissolved in warm benzene, and the solution dried ($MgSO_4$), boiled for 10 minutes with charcoal, filtered, and evaporated under reduced pressure. The *ester* was obtained as a brown oil (Found : C, 52·4; H, 4·1; Cl, 10·7. $C_{14}H_{12}O_2ClAs$ requires C, 52·1; H, 3·7; Cl, 11·0%). *Methyl diphenylchloroarsine*-4-*carboxylate* was similarly prepared and obtained as a pale brown oil (Found : C, 52·8; H, 4·0; Cl, 9·8%).

*Di*-o-*chlorophenylchloroarsine*.—The following conditions are based upon the Pope–Turner process for diphenylchloroarsine, communicated by the Ministry of Supply. A mixture of *o*-chlorophenyldichloroarsine (5·2 g.) and *o*-chlorophenylarsenious oxide (12·3 g.) was heated at 300° for an hour in an atmosphere of carbon dioxide, cooled, and treated with benzene. After removal of arsenious oxide by filtration, the benzene was distilled off under reduced pressure in an atmosphere of hydrogen. The residual *di*-o-*chlorophenylchloroarsine* solidified on cooling and, after crystallisation from petroleum, melted at 73—75° (Found : hydrolysable Cl, 10·3. $C_{12}H_8Cl_3As$ requires C, 43·2; H, 2·4; hydrolysable Cl, 10·6%).

The following were prepared by a similar process : di-*p*-chlorophenylchloroarsine, m. p. 45—48°, after being distilled and collected at 175—179°/0·6 mm. (Found : C, 43·4; H, 2·1; hydrolysable Cl, 10·4%) (cf. Hunt and Turner, *J.*, 1925, **127**, 2667); di-1-naphthylchloroarsine, m. p. 163—165° (cf. Challenger and Ridgway, *J.*, 1922, **121**, 104; Matsumiya and Nakai, *loc. cit.*; Blicke and Smith, *J. Amer. Chem. Soc.*, 1929, **51**, 1558); *di*-2-*naphthylchloroarsine*, colourless plates, m. p. 88°, from petroleum (b. p. 60—80°) (Found : Cl, 10·1. $C_{20}H_{14}ClAs$ requires Cl, 9·7%).

3-*Chloroacetyldiphenylchloroarsine*.—3-Acetyldiphenylchloroarsine was heated at 100° in a sealed tube with slightly more than one molecular proportion of chlorine in dry carbon tetrachloride solution in bright sunlight for several hours. After removal of the solvent under reduced pressure, 3-*chloroacetyldiphenylchloroarsine* remained as a viscous yellow oil (Found : hydrolysable Cl, 21·0. $C_{14}H_{11}OCl_2As$ requires hydrolysable Cl, 20·8%).

*Di*-2-*thienylchloroarsine*.—The following conditions proved to be much more satisfactory for this preparation than those described by Steinkopf (*loc. cit.*). A mixture of 2-thienylmercury chloride (600 g.), arsenic trichloride (180 g.), and toluene (1100 c.c.) was refluxed for 6 hours, cooled, and filtered from the precipitate of mercuric chloride. Most of the toluene and unchanged arsenic trichloride were removed from the filtrate by distillation under reduced pressure in an atmosphere of hydrogen from a flask fitted with a fractionating column. The residual oil (248 g.) was fractionally distilled (hydrogen atmosphere) at 13 mm. in seven separate portions to avoid prolonged heating and consequent disproportionation of the product. The following combined fractions were collected : (i) b. p. below 120° (13 g.), (ii) b. p. 120—125° (7·5 g., mostly 2-thienyldichloroarsine), (iii) b. p. 125—180° (36 g.), and (iv) b. p. 180—220° (130 g.). The last fraction, most of which boiled at 195—210°/13 mm., was a reasonably pure specimen of di-2-thienylchloroarsine (Found : Cl, 11·8. Calc. for $C_8H_6S_2ClAs$ : Cl, 12·8%). The residue was distilled at a lower pressure and gave an oil (40 g.), b. p. 195—200°/0·5 mm., which was mainly tri-2-thienylarsine.

For the preparation of purer tri-2-thienylarsine, a mixture of 2-thienyldichloroarsine and di-2-thienylchloroarsine was heated in toluene for 7 hours under reflux with excess of 2-thienylmercury chloride, and worked up as described above. A fraction, b. p. 180—194°/0·8 mm., containing 5·5% of chlorine, and another, b. p. 194—196°/0·8 mm., containing 0·8% of chlorine, were collected. These were united and heated for 5 minutes in alcohol at 70° with a little potassium hydroxide. After filtration, the alcohol was removed by distillation in steam, and the oily residue was washed by decantation with water and dissolved in ether. The solution was dried ($Na_2SO_4$), the solvent removed, and the residue fractionally distilled in an atmosphere of hydrogen. Tri-2-thienylarsine, almost free from chlorine, was collected at 193—198°/0·55 mm. as a practically colourless liquid (Found : C, 44·4; H, 3·1; Cl, 0·4; S, 31·2; As, 20·5. Calc. for $C_{12}H_9S_3As$ : C, 44·4; H, 2·8; S, 29·7; As, 23·2%).

*Phenyl-2-thienylchloroarsine.*—(*a*) A mixture of 2-thienylmercury chloride (10 g.), phenyldichloroarsine (7 g.), and toluene (20 c.c.) was boiled under reflux for 7 hours. After the solid which had separated had been removed by filtration and washed with toluene, the solvent was removed from the united toluene solutions under reduced pressure. The residue was distilled at a low pressure in an atmosphere of hydrogen, and two main fractions were collected. The first (1·7 g.), b. p. 93—106°/0·3 mm., was evidently phenyldichloroarsine, 2-thienyldichloroarsine, or a mixture of the two (Found : Cl, 32·0. Calc. for $C_6H_5Cl_2As$ : Cl, 31·8. Calc. for $C_4H_3Cl_2SAs$ : Cl, 31·0%). The second (3·5 g.) was collected at 158—172°/0·9 mm., and consisted essentially of *phenyl-2-thienylchloroarsine* (Found : C, 42·0; H, 2·9; Cl, 15·9. $C_{10}H_8ClSAs$ requires C, 44·4; H, 3·0; Cl, 13·1%). A small amount of less volatile material remained.

(*b*) A mixture of phenylmercury chloride (27 g., prepared as described by Roeder and Blasi, *Ber.*, 1914, **47**, 2748), 2-thienyldichloroarsine (19·5 g.), and toluene (50 c.c.) was boiled under reflux for 7 hours, and then treated as above. After a fraction (7 g.) of dichloroarsine type (Found : Cl, 31·4%) had been obtained at 96—112°/0·65 mm., phenyl-2-thienylchloroarsine (6 g.) was collected at 150—156°/0·7 mm. (Found : C, 41·0; H, 2·6; Cl, 15·3%). The analyses indicate a small amount of disproportionation to dichloroarsines during distillation.

### *Diarylcyanoarsines.*

Some of the cyanoarsines described below were isolated as solids and were purified by crystallisation, but those obtained as oils were usually not distilled owing to the possibility of disproportionation in accordance with the scheme, $2R_2As{\cdot}CN \rightleftarrows RAs(CN)_2 + R_3As$. Most of these liquids were shown by analysis to be reasonably pure, but, in a few, a low nitrogen content probably indicated the presence of a small amount of the corresponding oxide, RR′As·O·AsRR′, formed by hydrolysis.

*Phenyl-*o*-tolylcyanoarsine.*—Phenyl-*o*-tolylchloroarsine (15 g.) was added to a solution of sodium cyanide (2·9 g.) in water (6 c.c.), and the whole shaken vigorously for 10 minutes, the temperature being maintained at 60°. The resulting oil was extracted with ether, and, after the extract had been dried ($Na_2SO_4$) and filtered, the solvent was removed by distillation under reduced pressure from a water-bath. *Phenyl-*o*-tolylcyanoarsine* (11 g.) remained as a faintly red, viscous oil (Found : C, 61·9; H, 4·2; N, 5·2. $C_{14}H_{12}NAs$ requires C, 62·5; H, 4·5; N, 5·2%).

The following were similarly prepared : *phenyl-*p*-tolylcyanoarsine*, golden yellow liquid (Found : C, 63·2; H, 4·8; N, 4·7%); *2-chlorodiphenylcyanoarsine*, pale yellow oil, which solidified on standing and then melted at 40—42° (Found : C, 54·7; H, 3·4; N, 4·9. $C_{13}H_9NClAs$ requires C, 53·9; H, 3·1; N, 4·8%); *4-chlorodiphenylcyanoarsine*, m. p. 102° (Found : N, 4·8%); *phenyl-2-thienylcyanoarsine*, practically colourless oil, b. p. 168—174°/0·5 mm., which solidified on standing and then melted at 49—51° (Found : C, 49·5; H, 3·1; N, 4·4; S, 12·8. $C_{11}H_8NSAs$ requires C, 50·6; H, 3·1; N, 5·4; S, 12·3%).

*Di-*m*-tolylcyanoarsine.*—A suspension of di-*m*-tolylarsonous acid (7 g.) in concentrated hydrochloric acid (40 c.c.) at 90°, containing a little potassium iodide, was mechanically stirred while sulphur dioxide was passed in for 1½ hours. The oily di-*m*-tolylchloroarsine was extracted with carbon tetrachloride, and the extract dried ($MgSO_4$) and evaporated on the steam-bath under reduced pressure. The residue was dissolved in benzene (20 c.c.) and shaken with sodium cyanide (1·7 g.) in water (3·4 c.c.) at 40° for 10 minutes. The whole was filtered from sodium chloride, the aqueous layer removed, and the benzene solution dried ($MgSO_4$). When the benzene was removed on the steam-bath under reduced pressure, *di-*m*-tolylcyanoarsine* remained in good yield as a brownish yellow oil (Found : N, 5·0. $C_{15}H_{14}NAs$ requires N, 4·9%). The oil solidified on standing, and then melted again at 43—47°.

The following were similarly prepared : *phenyl-*m*-tolylcyanoarsine*, brownish yellow liquid (Found : N, 5·1%); *phenyl-*m*-4-xylylcyanoarsine*, viscous brown oil (Found : N, 4·6%); *di-*o*-tolylcyanoarsine*, colourless prisms, m. p. 74°, from petroleum (b. p. 40—60°) (Found : N, 5·2%); o*-tolyl-*m*-tolylcyanoarsine*, pale brown oil (Found : N, 4·1%); o*-tolyl-*p*-tolylcyanoarsine*, pale brown oil which solidified on standing (Found : C, 61·9; H, 4·8; N, 4·5. $C_{15}H_{14}NAs$ requires C, 63·6; H, 4·9%); m*-tolyl-*p*-tolylcyanoarsine*, reddish brown oil (Found : N, 4·5%); *di-*p*-tolylcyanoarsine*, colourless plates, m. p. 62°, with a faint pink tinge, from petroleum (b. p. 40—60°) (Found : N, 5·0%); o*-tolyl-*m*-4-xylylcyanoarsine*, brown oil (Found : N, 3·5. $C_{16}H_{16}NAs$ requires N, 4·7%); p*-tolyl-*m*-4-xylylcyanoarsine*, brown oil (Found : N, 3·7%); o*-chlorophenyl-*o*-tolylcyanoarsine*, colourless prisms, m. p. 69°, from petroleum (b. p. 40—60°) (Found : N, 4·5. $C_{14}H_{11}NClAs$ requires N, 4·6%); m*-chlorophenyl-*o*-tolylcyanoarsine*, colourless prisms, m. p. 61°, from petroleum (b. p. 40—60°) (Found : N, 4·8%); p*-chlorophenyl-*o*-tolylcyanoarsine*, colourless prisms, m. p. 64°, from petroleum (b. p. 40—60°) (Found : N, 4·8%); o*-chlorophenyl-*p*-tolylcyanoarsine*, brown oil (Found : N, 4·2%); m*-chlorophenyl-*p*-tolylcyanoarsine*, brown oil (Found : N, 4·2%); p*-chlorophenyl-*p*-tolylcyanoarsine*, brownish yellow oil (Found : N, 4·4%); o*-nitrophenyl-*o*-tolylcyanoarsine*, yellow prisms, m. p. 105—107°, from petroleum (b. p. 60—80°) (Found : N, 7·6. $C_{14}H_{11}O_2N_2As$ requires N, 8·9%); m*-nitrophenyl-*o*-tolylcyanoarsine*, colourless prisms, m. p. 99—101°, from benzene (Found : N, 8·9%); p*-nitrophenyl-*o*-tolylcyanoarsine*, colourless prisms, m. p. 103—105°, from benzene (Found : N, 8·9%); p*-nitrophenyl-*p*-tolylcyanoarsine*, pale yellow needles, m. p. 88—90°, from petroleum (b. p. 60—80°) (Found : N, 8·8%); *3-formyldiphenylcyanoarsine*, viscous, golden yellow oil (Found ; N, 4·6. $C_{14}H_{10}ONAs$ requires N, 4·9%); *3-acetyldiphenylcyanoarsine*, colourless prisms, m. p. 57—59°, from petroleum (Found : CN, 8·8. $C_{15}H_{12}ONAs$ requires CN, 8·8%); phenyl-1-naphthylcyanoarsine, yellow plates, m. p. 98—99°, from methyl alcohol (Found : N, 3·9%) (cf. Klippel, *loc. cit.*); *phenyl-2-naphthylcyanoarsine*, m. p. 59—61°, after crystallisation from petroleum

(b. p. 60—80°) (Found : N, 4·5. $C_{17}H_{12}NAs$ requires N, 4·6%) ; p-*tolyl*-1-*naphthylcyanoarsine*, colourless prisms, m. p. 83—84°, from benzene–petroleum (b. p. 60—80°) (Found : N, 4·4. $C_{18}H_{14}NAs$ requires N, 4·4%) ; p-*tolyl*-2-*naphthylcyanoarsine*, colourless prisms, m. p. 99°, from petroleum (b. p. 60—80°) (Found : N, 4·4%).

*Di*-o-*chlorophenylcyanoarsine*.—A solution of di-*o*-chlorophenylchloroarsine in the minimum quantity of benzene at 40° was vigorously shaken for 10 minutes at 50° with slightly more than one molecular proportion of sodium cyanide in concentrated aqueous solution. After the mixture had been cooled, sufficient water and benzene were added to give two clear layers. The benzene layer was washed with water, dried ($MgSO_4$), and filtered. When the solvent had been removed under reduced pressure in an atmosphere of hydrogen, *di*-o-*chlorophenylcyanoarsine* remained as an oil which soon solidified. After crystallisation from petroleum (b. p. 60—80°), it melted at 85—87° (Found : N, 4·1. $C_{13}H_8NCl_2As$ requires N, 4·3%).

The following were similarly prepared : *di*-p-*chlorophenylcyanoarsine*, b. p. 198—200°/0·5 mm., colourless prisms, m. p. 58—60°, from petroleum (b. p. 60—80°) (Found : CN, 7·6. $C_{13}H_8NCl_2As$ requires CN, 8·0%) ; *methyl diphenylcyanoarsine*-3-*carboxylate*, pale brown oil (Found : N, 3·6. $C_{15}H_{12}O_2NAs$ requires N, 4·5%) ; *methyl diphenylcyanoarsine*-4-*carboxylate*, pale brown oil (Found : N, 3·9%) ; di-1-naphthylcyanoarsine, colourless plates, m. p. 191°, from benzene (Found : N, 4·2%) (cf. Grichkiewitch-Trochimowski, Mateyak, and Zablotski, *Bull. Soc. chim.*, 1927, **41**, 1323) ; *di*-2-*naphthylcyanoarsine*, colourless prisms, m. p. 89—91°, from benzene–petroleum (b. p. 60—80°) (Found : N, 3·8. $C_{21}H_{14}NAs$ requires N, 3·9%).

2-*Aminodiphenylcyanoarsine*.—After a solution of 2-aminodiphenylarsonous acid (5 g.) in concentrated hydrochloric acid (100 c.c.) had been saturated with sulphur dioxide, the precipitated hydrochloride of 2-aminodiphenylchloroarsine (5·5 g.) was collected on a sintered glass filter, washed with hydrochloric acid, and dried. The hydrochloride (3·2 g.) was triturated for a few minutes with a cold solution of sodium cyanide (1·05 g.) in water (3 c.c.). A little benzene was added and trituration continued until the cyanoarsine had dissolved in the benzene layer, which was then separated, dried ($MgSO_4$), and evaporated under reduced pressure at room temperature. 2-*Aminodiphenylcyanoarsine* melted at 53° after recrystallisation from benzene, and was found to be hygroscopic (Found : CN, 8·9. $C_{13}H_{11}N_2As$ requires CN, 9·6%).

*Di*-m-*aminophenylcyanoarsine*.—When sulphur dioxide was passed into a solution of di-*m*-aminophenylarsonous acid (prepared as described by Blicke, Oakdale, and Oneto, *J. Amer. Chem. Soc.*, 1934, **56**, 141) in concentrated hydrochloric acid containing a little sodium iodide, the dihydrochloride of di-*m*-aminophenylchloroarsine was precipitated in almost quantitative yield. Sodium cyanide (3·1 molecular proportions) was added in small portions to a well-stirred suspension of the dihydrochloride in slightly more than its own weight of water below 30°. The mixture was diluted with its own volume of water, and stirring was continued for a further 5 minutes. The solid *di*-m-*aminophenylcyanoarsine* was filtered off, washed with water, and dried in a desiccator. After crystallisation from benzene, it was obtained in colourless plates, m. p. 114° (Found : CN, 9·3. $C_{13}H_{12}N_3As$ requires CN, 9·1%).

*Di*-2-*thienylcyanoarsine*.—Di-2-thienylchloroarsine (50 g.) was added in portions with vigorous shaking to a solution of sodium cyanide (10·5 g.) in water (21 c.c.), the temperature being kept between 17° and 25°. After the completion of the reaction, indicated by a fall in temperature, benzene (250 c.c.) was added, and the mixture filtered to remove sodium chloride. The benzene layer was shaken with an equal volume of water, dried ($MgSO_4$), and filtered. After the solvent had been removed from the filtrate, the residue was distilled under reduced pressure in an atmosphere of hydrogen. *Di*-2-*thienylcyanoarsine* (32 g.) was collected as an oil, b. p. 175—200°/0·3 mm., which rapidly solidified. On crystallisation from petroleum (b. p. 40—60°) it was obtained in colourless plates, m. p. 51—55° (Found : C, 39·3 ; H, 2·3 ; N, 5·2. $C_9H_6NS_2As$ requires C, 40·4 ; H, 2·2 ; N, 5·2%).

*Arsanthren Cyanide*, $C_6H_4{<}[AsCN]_2{>}C_6H_4$.—A mixture of arsanthren chloride (prepared from *o*-arsanilic acid as described by Kalb, *loc. cit.*) with 10 times its weight of dry toluene and freshly precipitated silver cyanide (50% excess) was refluxed for 10 hours. When the hot solution was filtered and left to cool, *arsanthren cyanide* separated. After recrystallisation from benzene, it was obtained in large, colourless prisms (dried under reduced pressure at room temperature) containing benzene of crystallisation (Found : C, 52·1 ; H, 2·7 ; N, 7·3. $2C_{14}H_8N_2As_2,C_6H_6$ requires C, 51·9 ; H, 2·8 ; N, 7·1%). When heated to constant weight under reduced pressure at 110—120°, the loss in weight amounted to 9·8% (Calc. : 9·9%), and arsanthren cyanide, m. p. 165—167°, was obtained free from benzene (Found : CN, 15·0. $C_{14}H_8N_2As_2$ requires CN, 14·7%).

p-*Phenylenebisdichloroarsine*.—Crude *p*-phenylenediarsonic acid, prepared essentially as described by Bart (*Annalen*, 1922, **429**, 55), was dissolved in hot alcohol which had been saturated with hydrogen chloride. The solution was cooled, filtered, treated with a few c.c. of hydriodic acid (*d* 1·7), saturated with sulphur dioxide, and left at room temperature for 2 days, during which time hydrogen chloride and sulphur dioxide were occasionally passed in. A small amount, m. p. 93—97°, of practically pure p-*phenylenebisdichloroarsine* separated and was removed, but the main product (m. p. 75—85°) was obtained by adding the filtrate to about an equal volume of water. After crystallisation from petroleum (b. p. 60—80°), it was obtained in practically colourless plates, m. p. 96—97° (Found : C, 19·9 ; H, 1·1 ; Cl, 37·5. $C_6H_4Cl_4As_2$ requires C, 19·6 ; H, 1·1 ; Cl, 38·6%). Kretow and Berlin (*Chem. Zentr.*, 1932, i, 3048) apparently used this substance to obtain the disulphide, $C_6H_4(AsS)_2$, but no details of its preparation or physical properties are given.

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