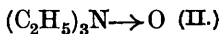
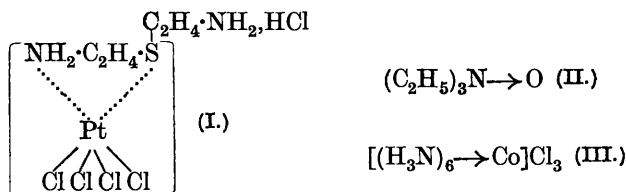


126. *The Polarity of the Co-ordinate Link. Part I.* *The Constitution of the Arsinimines.*

By FREDERICK GEORGE MANN.

EXPERIMENTAL evidence to confirm the assumption that in complex metallic salts the co-ordinated molecules of ammonia, water, organic sulphides, tertiary arsines, etc., were bound to the central metallic atom by "co-ordinate links" or "semipolar double bonds" was recently sought by the author, and for this purpose the optical resolution of tetrachloro-($\beta\beta'$ -diaminodiethyl sulphide monohydrochloride)platinum (I) was accomplished (Mann, J., 1930, 1745).



The optical activity of this compound is due to the asymmetric sulphur atom, and would indicate that the linkage between this atom and the platinum is the same as that between the sulphur and oxygen atoms in an organic sulphoxide, *i.e.*, a co-ordinate link. One alternative possibility, however, is that the sulphur atom is joined to the platinum by a "singlet link," which, having a fixed direction in space, would also confer asymmetry upon the sulphur atom and thus enable the compound to show optical activity.

The presence of singlet links in these complex metallic salts has been suggested by Sugden (J., 1929, 316) mainly for two reasons: (1) the experimental fact that the parachor of certain fusible metallic derivatives of acetylacetone agrees better with the value calculated on the assumption that singlet links, instead of co-ordinate links, are present in these compounds; and (2) the theoretical reason that the presence of a co-ordinate link in triethylamine oxide (II) gives a marked polarity to the nitrogen and oxygen atoms, which are thus able to exert a positive and a negative charge respectively: if the same linkage is present between the nitrogen atoms and the cobalt in hexamminocobaltic trichloride (III), the cumulative effect of these strongly polar links would be to give the cobalt atom a strongly electronegative charge. Actually the cobalt gives no evidence of such properties.

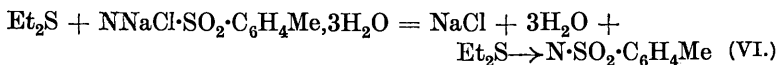
The best method of deciding whether co-ordinate or singlet links are present in these metallic salts would undoubtedly be a direct measurement of their parachor. The preparation of suitable com-

plex salts which, being either fusible without decomposition or alternatively soluble in non-ionic solvents, lend themselves to such measurements, is now being undertaken in this laboratory. Meanwhile, it was considered of interest to investigate experimentally the factors which influence the polarity of the co-ordinate link.

In the organic sulphoxides, *e.g.*, diethyl sulphoxide (IV), the oxygen atom is definitely bound to the sulphur by a co-ordinate link, as shown by the optical resolution of suitable sulphoxides by Harrison, Kenyon, and Phillips (J., 1926, 2079). This co-ordinate



link possesses a marked chemical polarity, since the sulphoxide combines with acids to give stable hydroxy-salts, nitric acid thus giving the hydroxynitrate (V). When diethyl sulphide is treated with chloramine-T, it is readily converted into diethylsulphine-*p*-toluenesulphonylimine (VI) (Mann and Pope, J., 1922, 121, 1052) :



here again the optical resolution of such sulphilimines by Clarke, Kenyon, and Phillips (J., 1927, 188) has shown that a co-ordinate link exists between the sulphur and the nitrogen atom. Yet in these sulphilimines the co-ordinate link shows no polar properties, and no record of the addition of other definitely polar molecules, *e.g.*, nitric acid, to this co-ordinate link has yet appeared.

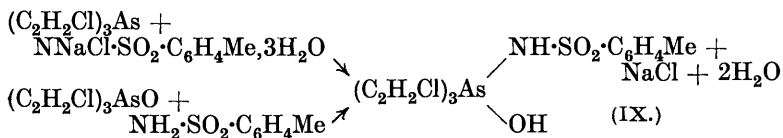
Attempts were therefore made to decide whether this striking loss of the polar properties of the co-ordinate link when the oxygen atom of the sulphoxides was replaced by the $:N \cdot SO_2 \cdot C_6H_4 \cdot Me$ group of the sulphilimines would extend to other similar compounds. In the tertiary arsine oxides, *e.g.*, tri-*p*-tolylarsenoxide (VII), the co-ordinate link between the arsenic and the oxygen atom possesses even more markedly polar properties than that in the sulphoxides.



Not only will the arsenoxide combine with a number of strong acids, to give hydroxy-salts, but it will also combine directly with water to give arsine dihydroxides, possessing marked stability. It was of interest, therefore, to determine whether, when a tertiary arsine was treated with chloramine-T, an arsinimine would result, *e.g.*, tri-*p*-tolylarsine-*p*-toluenesulphonylimine (VIII), in which the co-ordinate link between the arsenic and the nitrogen atom would be neutral, or whether the polar properties of the arsenoxide would reappear, diminished but still existent, in the new compound.

One such case had already been recorded by Mann and Pope

(J., 1922, 121, 1754), who showed that $\beta\beta'\beta''$ -trichlorotrivinylarsine on treatment with chloramine-T gave a compound of composition $(C_2H_2Cl)_3As \cdot N \cdot SO_2 \cdot C_6H_4Me, H_2O$. Since, however, this compound in benzene solution gave no effervescence with calcium carbide, it was inferred that the molecule of water was definitely bound to the organic molecule, which probably had the composition (IX). This proposed constitution has now been placed beyond doubt by the preparation of the same compound by the direct union of $\beta\beta'\beta''$ -trichlorotrivinylarsenoxide and *p*-toluenesulphonamide. The compound is therefore definitely the hydroxysulphonamide of the tertiary arsine :—

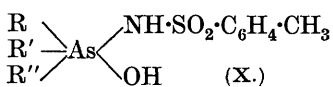


Precisely similar results have also been obtained with the three isomeric tri-*o*-, tri-*m*-, and tri-*p*-tolylarsines. Each reacts with chloramine-T to give the corresponding *tritolyarsinehydroxy-p-toluenesulphonamide*, $(C_7H_7)_3As(OH) \cdot NH \cdot SO_2 \cdot C_6H_4 \cdot Me$, which in all three cases can be synthesised alternatively by the direct union of the respective tritolyarsenoxide, or arsinedihydroxide, with *p*-toluenesulphonamide.

The interpretation placed originally on these results was that the chloramine-T first converted the arsine into a true arsinimine of type (VIII), a reaction precisely similar to the formation of a sulphilimine, and that the co-ordinate link between the arsenic and the nitrogen atom in this arsinimine then possessed sufficiently polar properties to unite with a molecule of water (always present in the hydrated chloramine-T used) to form the hydroxysulphonamide. The alternative explanation, now considered the more probable, is that the chloramine-T acts solely as an oxidising agent, converting the tertiary arsine into the arsenoxide (VII), and that it is the strongly polar co-ordinate link between the arsenic and the oxygen atom in the oxide that causes its direct union with the acidic *p*-toluenesulphonamide.

An objection originally held to this second explanation was that the chloramine-T, if it oxidised the tertiary arsine so readily to the arsenoxide, might reasonably be expected to oxidise sulphides similarly to sulphoxides, whereas actually it appeared always to convert sulphides directly into sulphilimines. This objection disappeared when it was found that some compounds of the chloramine-T class, *e.g.*, the phenyl analogue, $C_6H_5 \cdot SO_2 \cdot NNaCl, 3H_2O$, did convert certain sulphides into sulphoxides without any apparent

formation of sulphilimines. Further and more decisive evidence for the second, or direct oxidation, theory was obtained by the discovery that certain tertiary arsines when treated with chloramine-T did actually give the corresponding arsenoxides, and that the latter either definitely did not then combine with *p*-toluenesulphonamide, or alternatively gave a hydroxysulphonamide so sensitive to water that it underwent complete dissociation to arsenoxide and sulphonamide under the conditions of the experiment. The number of compounds investigated is insufficient to establish a general rule, but it would appear that when a tertiary arsine has one or more methyl groups directly attached to the arsenic atom, the action of chloramine-T is always to give the corresponding arsenoxide, which undergoes no apparent further change. This point arose during an investigation into the stereochemistry of these hydroxysulphonamides. It will be seen that if an asymmetric

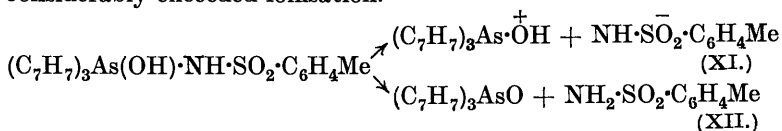


arsine is converted into the hydroxysulphonamide (X), the latter will possess molecular dissymmetry, and, if the group R possess acidic or basic

properties for salt formation, should be resolvable into optically active forms. This resolution, however, would probably have to be performed in non-ionising solvents, otherwise the ionisation of the toluenesulphonamido-group, which is directly attached to the arsenic atom, would probably cause very rapid, if not instantaneous, racemisation (Mills and Raper, J., 1925, 127, 2479). For this purpose, both *o*-carboxydiphenylmethylarsine, $\text{AsMePh}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})$ (Aeschlimann, *ibid.*, p. 812), and the isomeric *p*-compound, were treated with chloramine-T, but in each case only the corresponding arsenoxide, and not the hydroxysulphonamide, was obtained. Similarly phenyldimethylarsine with chloramine-T gave the arsenoxide, whilst the diethyl homologue behaved normally, giving phenyldiethylarsinehydroxy-*p*-toluenesulphonamide. Phenyl-(β -phenylethyl)methylarsine, $\text{AsMePh}(\text{CH}_2\cdot\text{CH}_2\cdot\text{Ph})$, again gave only the arsenoxide and toluenesulphonamide. Tribenzylarsine behaved peculiarly in giving a mixture of the arsenoxide and dibenzylarsonic acid, but this result may have been partly due to the unstable nature of tribenzylarsine itself. The production of the dibenzyl derivative recalls the ready conversion of disubstituted monochloroarsines into arsonic acids by chloramine-T (Burton and Gibson, J., 1924, 125, 2275). In view of these difficulties, and the possible rapid racemisation of the final product, no further attempt to prepare dissymmetric hydroxysulphonamides was made.

The hydroxysulphonamides now described represent a new class of arsenic compound, since structurally similar salts have previously

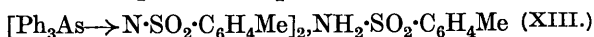
been obtained only by the union of arsenoxides with inorganic acids and the stronger organic acids, and not with acid amides. The general properties of tri-*p*-tolylarsinehydroxy-*p*-toluenesulphonamide were therefore studied in some detail. It was expected, in view of the feebly acidic nature of *p*-toluenesulphonamide, that this compound would undergo only slight ionisation in solution (equation XI), and that this ionisation would be further reduced by simultaneous molecular dissociation (equation XII). This was confirmed experimentally, since the molecular conductivity in alcohol proved to be very small. On the other hand, the molecular weight of the compound in ionising solvents, such as acetone and acetonitrile, indicated considerable dissociation: since, however, the molecular weight in boiling chloroform, and even in dilute toluene, was also low, it is probable that in all these solvents molecular dissociation considerably exceeded ionisation.



When the hydroxysulphonamide in cold alcoholic solution was treated with picric acid, *tri-p-tolylarsine hydroxypicrate*, $(\text{C}_7\text{H}_7)_3\text{As}(\text{OH})\cdot\text{O}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, rapidly separated: moreover, when the hydroxysulphonamide was treated either directly or in alcoholic solution with sodium hydroxide, tri-*p*-tolylarsenoxide and the sodium derivative of *p*-toluenesulphonamide were formed. Both these reactions, however, can be explained on the basis of ionisation, or molecular dissociation, of the original hydroxysulphonamide.

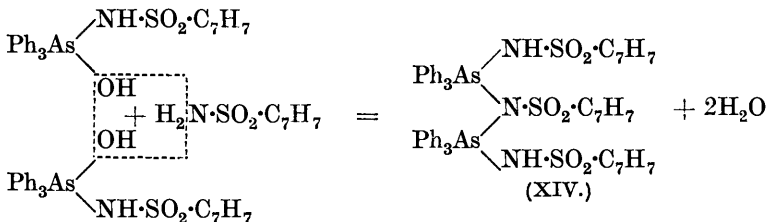
Precisely similar results were obtained with tri-*m*-tolylarsinehydroxy-*p*-toluenesulphonamide.

The present investigation throws further light on the constitution of the highly stable, crystalline compound which Mann and Pope obtained by the action of chloramine-T on triphenylarsine; it has m. p. 175—176°, and its composition corresponds to 2 mols. of a true arsinimine, *viz.*, triphenylarsine-*p*-toluenesulphonylimine, combined with 1 mol. of *p*-toluenesulphonamide:



This compound has been reinvestigated in detail, and is found always to be formed whenever triphenylarsine is treated with chloramine-T, or triphenylarsenoxide with *p*-toluenesulphonamide, even if the comparative amounts of the two reagents are varied in each case over wide limits. Moreover, the compound is easily hydrolysed by cold sodium hydroxide solution, giving triphenylarsenoxide and *p*-toluenesulphonamide: when treated in alcoholic solution

with picric acid, it readily yields triphenylarsine hydroxypicrate. The action of chloramine-T on triphenylarsine must undoubtedly be first to give triphenylarsenoxide and *p*-toluenesulphonamide, which to a certain extent combine normally to give triphenylarsine-hydroxysulphonamide : 2 mols. of the latter under the conditions of the experiment then condense with one of the free sulphonamide to give the less soluble trisulphonamido-derivative (XIV). The



latter is therefore akin in its general constitution to arsenimide, $\text{NH}\cdot\text{As}\cdot\text{NH}\cdot\text{As}\cdot\text{NH}$, and there is no evidence for the presence of the co-ordinate link shown in (XIII). Molecular-weight determinations gave no decisive evidence with regard to the constitution of this compound : its low solubility in cold solvents necessitated the employment of the ebullioscopic method, and at the high temperatures thus involved the compound probably underwent both dissociation and ionisation, the results indicating an apparent splitting into 3, 4, and 5 particles in various solvents. When triphenylarsine was treated with benzenesulphonchlorosodioamide, however, it was converted normally into triphenylarsinehydroxy-benzenesulphonamide, $\text{Ph}_3\text{As}(\text{OH})\cdot\text{NH}\cdot\text{SO}_2\text{Ph}$.

Whilst this investigation was in progress, the author's attention was drawn by Dr. H. McCombie to some unpublished results which the late Mr. A. C. P. Lunn and he had obtained with $\beta\beta'$ -dihydroxy-diethyl sulphide, or thiodiglycol. This compound reacts with chloramine-T to give a *sulphilimine*, $(\text{C}_2\text{H}_4\cdot\text{OH})_2\text{S}\rightarrow\text{N}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7, \text{H}_2\text{O}$. The molecule of water is firmly fixed in this compound and, as in the case of the trichlorotriphenylarsine compound already mentioned, is not detached when the substance is treated in hot benzene solution with calcium carbide. It appeared, therefore, that this sulphilimine was peculiar in that the co-ordinate link between the sulphur and the nitrogen atom was sufficiently polar to cause the direct addition of water to give a hydroxy-sulphonamide,



similar to the arsenic compounds already described. To confirm this constitution, many experiments were performed to determine whether *p*-toluenesulphonamide would combine directly with $\beta\beta'$ -dihydroxydiethyl sulphoxide, a supply of which was kindly

furnished by Dr. McCombie. In spite of wide variations in temperature, solvent, etc., no indication of such combination was obtained, however, and the constitution of this peculiar hydrated sulphilimine remains uncertain. It was found, too, that thiodiglycol behaves abnormally in other respects, since when treated even in ice-cold aqueous solution with benzenesulphonchlorosodioamide, it was rapidly converted into dihydroxydiethyl sulphoxide, with the simultaneous formation of benzenesulphonamide. This result was not due to inability of the benzenesulphonchlorosodioamide to give a sulphilimine, since the former when treated with diethyl or methyl ethyl sulphide readily gave normal sulphilimines such as *diethylsulphinebenzenesulphonylimine*, $(C_2H_5)_2S \longrightarrow N \cdot SO_2 \cdot C_6H_5$.

Some preliminary experiments tend to show that the diaryl tellurides when treated with chloramine-T give hydroxysulphonamides, their behaviour thus resembling that of the arsines, and not that of the sulphides.

EXPERIMENTAL.

$\beta\beta'\beta''$ -*Trichlorotrivinylarsinehydroxy-p-toluenesulphonamide* (IX).—The preparation of this compound by the action of chloramine-T on the tertiary arsine has already been described (Mann and Pope, *loc. cit.*). Alternatively, $\beta\beta'\beta''$ -trichlorotrivinylarsenoxide (2 g.) and *p*-toluenesulphonamide (1.3 g.) were added to anhydrous benzene (18 c.c.), and the mixture heated under reflux for 30 minutes. The clear solution on cooling gave colourless crystals, which, when washed with benzene and dried, had m. p. 122—123°, unchanged by admixture with the compound obtained as above.

Tri-p-tolylarsinehydroxy-p-toluenesulphonamide (as X).—Solutions of *tri-p*-tolylarsine (5 g.) and of chloramine-T (6 g.; 1.5 mols.), each in hot absolute alcohol (200 c.c.), were mixed, a fine precipitate of sodium chloride rapidly separating. The liquid was boiled under reflux for 3 hours, filtered from sodium chloride, and evaporated to a thick syrup. When the cold syrup was stirred with dry ether, it rapidly formed a mass of white crystals; these, twice recrystallised from benzene, had m. p. 137—138° (Found: C, 62.8; H, 5.6; N, 2.85; S, 6.05. $C_{28}H_{30}O_3NSAs$ requires C, 62.8; H, 5.6; N, 2.6; S, 6.0%).

Tri-p-tolylarsine dihydroxide (2 g.), made by the method of Michaelis (*Annalen*, 1902, **321**, 202), and *p*-toluenesulphonamide (0.9 g.) were added to anhydrous benzene (20 c.c.). The clear solution obtained by 15 mins.' heating under reflux gave on cooling crystals of m. p. 137—139°, unchanged by admixture with the foregoing compound.

The *hydroxysulphonamide* is freely soluble in cold alcohol and

acetone, and in boiling benzene, but only slightly soluble in boiling ether. It is also very slightly soluble in boiling water, from which it crystallises unchanged on slow cooling. The following table gives the values obtained for M , the molecular weight, by the ebullioscopic method, g being the weight in g. of solute in 100 g. of solvent (M , calc., = 517.3) :

	Acetone.		Acetonitrile.		Chloroform.		Toluene.	
M	342	368	215	225	318	320	496	543
g	5.089	11.81	5.392	9.219	2.602	4.468	5.070	8.820

A 3.745% alcoholic solution at 18° had a specific conductivity of 4.81×10^{-6} , and therefore a molecular conductivity of 0.0508, since the specific conductivity of the alcohol alone was 1.13×10^{-6} .

A cold alcoholic solution of the hydroxysulphonamide was treated with a 15% aqueous solution of sodium hydroxide : after 1 hour, the clear solution was diluted carefully with water. The fine emulsion so obtained rapidly precipitated crystalline tri-*p*-tolylarsine dihydroxide, m. p. 95—96°, unchanged by admixture with a known sample. After removal of the dihydroxide and acidification, the mother-liquor deposited *p*-toluenesulphonamide. Similar results were obtained when the hydroxysulphonamide was triturated directly with concentrated sodium hydroxide solution.

When the hydroxysulphonamide was treated with picric acid, each in cold alcoholic solution, yellow needles of *tri-p*-tolylarsine hydroxypicrate separated : these had m. p. 184—185° (decomp.), unchanged by recrystallisation from alcohol (Found : N, 7.15. $C_{27}H_{24}O_8N_3As$ requires N, 7.1%).

Tri-m-tolylarsinehydroxy-p-toluenesulphonamide.—This preparation from tri-*m*-tolylarsine was precisely similar to that of the *p*-compound. The syrup obtained by evaporation of the alcohol readily solidified on cooling, and the colourless crystals, when washed with ether and recrystallised from benzene, had m. p. 140—141.5° (Found : C, 62.8; H, 5.6; N, 2.8; S, 6.15%). Tri-*m*-tolylarsine dihydroxide also united rapidly with one equivalent of *p*-toluenesulphonamide in hot benzene solution to give the same compound, m. p. 140—142°, its identity being again confirmed by mixed m. p. determinations.

Molecular-weight determinations, as for the previous compound, gave :

	Acetone.		Acetonitrile.			Chloroform.			Toluene.	
M	311	350	246	271	273	335	339	338	472	546
g	5.301	10.08	7.807	12.25	15.14	3.090	5.595	7.798	4.914	8.405

A 4.324% alcoholic solution at 18° had a specific conductivity of 7.94×10^{-6} , and therefore a molecular conductivity of 0.0815, the conductivity of the alcohol alone being as before.

Tri-o-tolylarsinehydroxy-p-toluenesulphonamide.—Tri-*o*-tolylarsine, m. p. 98°, was first prepared by Burrows and Turner (J., 1920, 117, 1382). The preparation was repeated, and the arsine, when thrice recrystallised from absolute alcohol, had m. p. 108–109°. Analysis showed it to be pure. This arsine (15 g.) and chloramine-T (18.3 g.) were added to hot alcohol (400 c.c.), and the whole boiled under reflux for 5 hours. Sodium chloride was filtered off, and the alcohol evaporated until a viscous syrup remained. This was left in a vacuum for several days and then dissolved in hot benzene. On cooling, *p*-toluenesulphonamide crystallised in quantity. This was separated, and the benzene evaporated to small bulk. Dilution of the cold concentrated solution with anhydrous ether gave a crop of colourless crystals: these were purified by redissolution in benzene and reprecipitation with ether, and finally by two recrystallisations from benzene. The *hydroxysulphonamide* softened at 96° and melted at 98–104° (Found: C, 62.8; H, 5.8; S, 5.9%).

Action of Chloramine-T on o-Carboxydiphenylmethylarsine.—Solutions of the tertiary arsine (8 g.) and of chloramine-T (10 g., 1.25 mols.), each in hot alcohol (70 c.c.), were mixed, and boiled under reflux for 4 hours. The solution was filtered, evaporated to small bulk, and the semi-solid cold product washed with ether and then water. The white residue when dry was twice recrystallised from absolute alcohol, and then had m. p. 237–239°. The tertiary arsine had thus been converted into the arsenoxide, m. p. 242° (Aeschlimann, *loc. cit.*) (Found: C, 55.15; H, 4.35. Calc. for $C_{14}H_{13}O_3As$: C, 55.3; H, 4.3%).

Synthesis of p-Carboxydiphenylmethylarsine.—Benz-*p*-arsinic acid, $CO_2H \cdot C_6H_4 \cdot As(OH)_2$. *p*-Nitrobenzoic acid was reduced to *p*-aminobenzoic acid, and the latter converted into benz-*p*-arsonic acid (Lewis and Cheetham, *J. Amer. Chem. Soc.*, 1921, 43, 2119). The latter acid (20 g.) and hydriodic acid of constant b. p. (12.5 c.c.) were dissolved in turn in hot water (300 c.c.), and the filtered solution maintained at 70° whilst subjected to a rapid current of sulphur dioxide for 1 hour. The solution was chilled and the precipitated arsenic acid filtered off, dissolved in sodium carbonate, and reprecipitated with dilute sulphuric acid. The benz-*p*-arsinic acid was now pure enough for synthetic work, but could be further purified by dissolving it in a large volume of boiling water, from which on slow cooling it separated in large colourless leaflets, which do not melt below 300° (Found: C, 36.95; H, 3.2. $C_7H_7O_4As$ requires C, 36.55; H, 3.1%).

This compound was further characterised by warming it with concentrated hydriodic acid, and then adding alcohol until a clear solution was obtained. On slow cooling, benz-*p*-arsenious hydroxy-

iodide, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{As}(\text{OH})\text{I}$, separated as a yellow powder, which, when washed with alcohol and water and dried, had m. p. $92-94^\circ$ (Found : I, 37.0. $\text{C}_7\text{H}_6\text{O}_3\text{IAs}$ requires I, 37.35%).

p-Carboxyphenylmethyliodoarsine, $\text{AsMeI}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})$. Finely powdered benz-*p*-arsinic acid (15 g.) was added to a solution of sodium hydroxide (9 g.) in water (18 c.c.). When solution was almost complete, methyl alcohol (90 c.c.) and methyl iodide (6 c.c.) were added, and the mixture was kept under reflux without heating for 2 days. The solution was filtered to remove a brown sludge, and then evaporated to about one-third of its original bulk. A mixture of approximately equal volumes of dilute hydrochloric acid (1:1 by vol.) and concentrated potassium iodide solution was added to the cold residue until the latter was just acid, and a vigorous current of sulphur dioxide then passed through the chilled product. The heavy brownish-yellow precipitate was filtered off, washed with an aqueous solution of sulphur dioxide, dried, and recrystallised from benzene and then from methyl alcohol. The canary-yellow crystalline *iodo-arsine* thus obtained shrank at 165° and melted at $173-175^\circ$ (decomp.) (Found : C, 28.5; H, 2.4; I, 37.8. $\text{C}_8\text{H}_8\text{O}_2\text{IAs}$ requires C, 28.4; H, 2.4; I, 37.55%).

p-Carboxydiphenylmethylarsine, $\text{AsMePh}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})$. To obtain this compound from the *iodo-arsine*, the latter must be treated with at least 4 equivs. of phenylmagnesium bromide, otherwise much remains unchanged. The Grignard reagent, prepared by the action of bromobenzene (19.0 c.c.) on magnesium (4.4 g.) in ether (250 c.c.), was cautiously added with shaking to a fine suspension of the *iodo-arsine* (15 g.) in anhydrous benzene (100 c.c.). The first few drops of the Grignard reagent caused the *arsine* to dissolve, but the solution rapidly gave a yellow precipitate, presumably an additive product of the magnesium compound and the *arsine*. The final mixture was boiled under reflux for 30 minutes, the ether then distilled off, and the boiling of the benzene continued for another 3 hours. The product was then evaporated to dryness in an open dish, finely powdered, mixed with cold water, and filtered. The residue was washed with much dilute sulphuric acid, then with water, and dried. Recrystallisation from benzene gave the *arsine* as white crystals, m. p. $155-157^\circ$, which, when heated at 110° in a vacuum, sublimed unchanged as colourless needles (Found : C, 57.9; H, 4.5. $\text{C}_{14}\text{H}_{13}\text{O}_2\text{As}$ requires C, 58.3; H, 4.5%).

Action of Chloramine-T on p-Carboxydiphenylmethylarsine.—A solution of the *arsine* (2 g.) in hot alcohol (20 c.c.) was added to one of chloramine-T (1.9 g.) in alcohol (40 c.c.), sodium chloride being rapidly precipitated. The solution was boiled under reflux for 2 hours, filtered, and evaporated to half-bulk. On cooling, a

copious white precipitate formed : this was filtered, washed with ether and water, dried, and recrystallised from ethyl alcohol. The white crystalline *p*-carboxydiphenylmethylarsenoxide, when finally dried by heating at 110° in a vacuum, had m. p. 272—273° (Found : C, 55.0; H, 4.1. $C_{14}H_{13}O_3As$ requires C, 55.3; H, 4.3%).

Action of Chloramine-T on Phenyl dimethylarsine.—Several experiments were carried out in which these substances were mixed in either alcoholic or acetone solution. Boiling gave the usual precipitation of sodium chloride : when this was filtered off and the solution evaporated, a heavy viscous syrup was obtained. The latter when placed in a vacuum for several days gave a brittle glassy solid, which, however, could not be recrystallised. The syrup was apparently unaffected by repeated washings with anhydrous ether, and therefore could not contain free *p*-toluenesulphonamide, which is freely soluble in ether. When, however, it was treated with water, an immediate separation of *p*-toluenesulphonamide occurred, and the aqueous filtrate was found to contain the free arsenoxide. It is probable, therefore, that the syrup contained an unstable hydroxy-sulphonamide of the tertiary arsine, which was immediately hydrolysed by water. The identity of the arsenoxide obtained from the aqueous filtrate was confirmed by a direct preparation. For this purpose an alcoholic solution of phenyl dimethylarsine was treated with concentrated aqueous hydrogen peroxide solution, and the mixture slowly evaporated until a syrup was obtained. The latter when placed in a vacuum over phosphoric oxide gave an extremely deliquescent, brittle, white solid. The only suitable solvent for recrystallisation was boiling xylene, from which the *phenyl dimethylarsenoxide* separated in heavy colourless crystals, m. p. 159—161°. The recrystallisation and the subsequent filtration must be performed rapidly (Found : C, 48.1; H, 5.5. $C_8H_{11}OAs$ requires C, 48.5; H, 5.55%).

Phenyldiethylarsine hydroxy-p-toluenesulphonamide (as X).—The arsine (5.1 g.), dissolved in acetone (20 c.c.), was added to a solution of chloramine-T (6.8 g.) in hot acetone (170 c.c.). After an hour's boiling under reflux, the sodium chloride was filtered off, and the solution evaporated to small bulk. The solid product, when twice recrystallised from benzene, gave the *hydroxysulphonamide* as white crystals, m. p. 100—103° (Found : C, 51.2; H, 6.1. $C_{17}H_{24}O_3NSAs$ requires C, 51.4; H, 6.1%).

Phenyl-(β -phenylethyl)methylarsine when boiled in alcoholic solution with chloramine-T rapidly gave the usual precipitate of sodium chloride. When the latter was removed and the alcohol evaporated, there remained a thick syrup which could not be crystallised : treatment of the syrup with water caused the immediate

separation of *p*-toluenesulphonamide, the aqueous solution then containing apparently a very soluble arsenoxide.

Action of Chloramine-T on Tribenzylarsine.—Hot solutions of tribenzylarsine (5 g.) in alcohol (200 c.c.) and of chloramine-T (6 g., 1.5 mols.) in alcohol (80 c.c.) were mixed, and boiled under reflux for 1½ hours. The solution was filtered, evaporated to about 60 c.c., and allowed to cool, crystals of dibenzylarsonic acid then separating. These, when filtered off, washed with water, and twice recrystallised from alcohol, had m. p. 210—213° (Found : C, 57.8; H, 5.1. Calc. for C₁₄H₁₅O₂As : C, 57.9; H, 5.2%). The original filtrate was gently boiled, and then diluted with a little hot water; cooling gave a heavy oil, which finally solidified. The solid product was filtered, and twice recrystallised from hot 50% aqueous alcohol: tribenzylarsenoxide was thus obtained, having m. p. 228—230° (Found : C, 69.2; H, 5.85. Calc. for C₂₁H₂₁OAs : C, 69.2; H, 5.8%).

Chloramine-T thus provides a convenient method of preparing tribenzylarsenoxide of great purity, since Michaelis and Paetow (*Annalen*, 1886, **233**, 60) give m. p. 219—220°. If the arsenoxide alone is required, it is best to work in aqueous solution. For instance, a solution of chloramine-T (4.8 g.) in hot water (700 c.c.) was added to finely powdered pure tribenzylarsine, and the mixture boiled for 1½ hours, by which time it was clear. The solution, when allowed to cool slowly, deposited long needles of the arsenoxide (2.7 g.), again of m. p. 228—230°.

Derivative of Triphenylarsine and Chloramine-T.—In the original description of the preparation and properties of this compound (Mann and Pope, *loc. cit.*), it was stated that, although consistent analytical values for carbon could not be obtained, the values for other elements corresponded to the formula (XIII), *i.e.*, to C₅₇H₅₃O₆N₃S₃As₂. Many preparations have since been carried out always giving the same compound, melting sharply at 175—176°. Repeated analyses for carbon again failed to give consistent values, in spite of all the experimental precautions taken: analyses for hydrogen, nitrogen, sulphur, and arsenic, however, always gave consistent values in complete agreement with the above formula. The molecular weight, as found by the ebullioscopic method, was: in ethylene dibromide, 399; toluene, 391; acetone, 284; chloroform, 280; acetonitrile, 221; benzonitrile, 211; alcohol, 196. These values represent the mean of several determinations, but the results for each solvent varied over very narrow limits. C₅₇H₅₃O₆N₃S₃As₂ requires *M*, 1122; dissociation into 3 units gives an apparent molecular weight of 374; into 4 units, 280; into 5 units, 224.

When benzene solutions of triphenylarsine dihydroxide and

p-toluenesulphonamide were mixed and boiled under reflux, this compound was again formed, and, being much less soluble in boiling benzene than the other hydroxy-sulphonamides, crystallised out during the operation unless the solution was very dilute. Its identity with the former compound was confirmed by mixed m. p. determinations, and by analyses for nitrogen, sulphur, and arsenic. It is also far more soluble in boiling water than the other compounds investigated, and recrystallises well provided not more than 0.8 g. be taken in 100 g. of water.

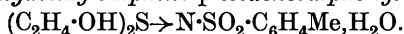
When a cold alcoholic solution of the substance was treated with picric acid, a crystalline precipitate of triphenylarsine hydroxypicrate rapidly separated; m. p. 166—167° (decomp.), unchanged by admixture with the picrate obtained directly from triphenylarsine dihydroxide. Steinkopf and Schwen (*Ber.*, 1921, 54, 2800) give the m. p. of the hydroxypicrate as 162—163°.

For hydrolysis, the finely powdered compound was triturated in a mortar with cold 15% aqueous sodium hydroxide solution. The bulk of the material diminished considerably, and after a few minutes the whole set rapidly to a thick cream. This was filtered off, and the solid residue well washed with sodium hydroxide solution and then with water. The filtrate was treated with hydrochloric acid, which rapidly precipitated *p*-toluenesulphonamide. The solid residue was dried and recrystallised from benzene. The crystals so obtained softened at 110—115°, and melted at 190—192°, and were evidently triphenylarsine dihydroxide. Their identity was confirmed by confinement in a vacuum over phosphoric anhydride for two days, whereby they were converted by dehydration into triphenylarsenoxide, m. p. 191—193° (Found: C, 66.8; H, 4.7. Calc. for $C_{18}H_{15}OAs$: C, 67.1; H, 4.7%).

Triphenylarsinehydroxybenzenesulphonamide.—Solutions of triphenylarsine (5 g.) and benzenesulphonchlorosodioamide (3.9 g.), each in hot alcohol (45 c.c.), were mixed and boiled under reflux for one hour. The solution was filtered from sodium chloride, and then gently evaporated until the residue solidified on cooling. The product was washed with ether, and then recrystallised first from alcohol and then from benzene, giving the *hydroxysulphonamide* as white crystals, m. p. 151—153° (Found: C, 60.0; H, 4.6; S, 6.6. $C_{24}H_{22}NO_3SA$ s requires C, 60.1; H, 4.6; S, 6.7%). The compound is slightly soluble in boiling water, and separates from very dilute solution on slow cooling in long needles. If the hot solution is nearly saturated, or is rapidly cooled, the material separates as an emulsion which finally deposits an oil.

The following two preparations were carried out by Dr. H. McCombie and Mr. A. C. P. Lunn.

“ $\beta\beta'$ -Dihydroxydiethylsulphine-*p*-toluenesulphonylimine,



—Aqueous solutions of thiodiglycol and chloramine-T (1 mol.) were mixed and kept at room temperature for 1 day. The solution was then evaporated under reduced pressure on a water-bath to a syrup, which solidified on cooling, and when recrystallised from chloroform containing a trace of alcohol, gave the above *sulphilimine* as white crystals, m. p. 86—88°. Further recrystallisation from acetone did not alter the m. p. or the composition (Found : C, 42·65; H, 6·1. $C_{11}H_{19}O_5NS_2$ requires C, 42·7; H, 6·1%). A solution of the sulphilimine in hot benzene was unaffected by the addition of a fragment of calcium carbide, indicating an absence of true water of crystallisation.

$\beta\beta'$ -Dihydroxydiethyl Sulphoxide.—Thiodiglycol dissolved in acetone was treated with a concentrated solution of hydrogen peroxide in aqueous acetone. The temperature rose rapidly, but by external cooling was not allowed to exceed 50°. The excess of peroxide was finally destroyed by colloidal platinum, and the solution evaporated under reduced pressure on a water-bath. The solid product was then recrystallised from alcohol, and the *sulphoxide* obtained in heavy white needles, m. p. 110—111° (Found : C, 34·5; H, 7·2. $C_4H_{10}O_3S$ requires C, 34·6; H, 7·3%).”

Many experiments were carried out in which equimolecular quantities of the sulphoxide and of *p*-toluenesulphonamide were heated in alcoholic and in acetone solutions, but no indication of combination was obtained, the two components being subsequently isolated unchanged. It was thought that the addition product might have been unstable at the temperature of the boiling solvents, although this was unlikely in view of the recorded recrystallisation of the sulphilimine. Similar mixtures were therefore dissolved at room temperature in alcoholic acetone, and the solvent allowed to evaporate spontaneously: again no sign of combination was obtained. Alternatively, the finely powdered mixture of sulphoxide and sulphonamide was heated without a solvent to 110—115°, and the resultant liquid maintained at this temperature for 30 minutes. When the product was allowed to cool and crystallise, however, no sign of chemical change could be detected.

Action of Benzenesulphonchlorosodioamide on Thiodiglycol.—Initial experiments in which the two substances were allowed to react in hot alcoholic solution showed that the sulphide was merely oxidised to the sulphoxide, with the formation of benzenesulphonamide. To check this oxidation if possible, a much lower temperature was used, and for this purpose aqueous solutions had necessarily to be employed. Cold solutions of the sulphide (5·6 g.) and

the chloro-amide (10.8 g.), in 50 c.c. and 100 c.c. of water respectively, were mixed, and the temperature kept below 14° by external cooling. White crystals rapidly separated, and after 4 hours were filtered off, washed with water and dried: they then had m. p. 150—152°, and were proved to be benzenesulphonamide (mixed m. p.). The original filtrate was then concentrated by evaporation, first at low temperature and strongly reduced pressure, and then in a desiccator to a thick syrup containing crystals of sodium chloride. When this syrup was recrystallised from much boiling acetone, thiodiglycol sulphoxide, m. p. 110—113°, was obtained, and again identified by mixed m. p. determinations.

Diethylsulphinebenzenesulphonylimine (as VI).—Diethyl sulphide (4.8 g.) was added to a cold solution of benzenesulphonchlorosodiumamide (18.9 g., 1.5 mols.) in water (200 c.c.). The mixture when shaken became warm, and white crystals rapidly separated. The product, after being shaken for 6 hours, was filtered, washed with water, dried, and recrystallised from alcohol. The *sulphilimine* was then obtained in white crystals, m. p. 114—116° (Found: N, 5.75; S, 26.4. $C_{10}H_{15}O_2NS_2$ requires N, 5.7; S, 26.15%). The same product was obtained when the reaction was carried out in hot alcoholic solution.

Methylethylsulphinebenzenesulphonylimine.—The preparation of this compound was precisely similar to that of the previous substance, although the product did not separate so rapidly from aqueous solution. Recrystallisation from benzene gave the *sulphilimine* as colourless crystals, m. p. 92—94° (Found: N, 6.3; S, 28.0. $C_9H_{13}O_2NS_2$ requires N, 6.1; S, 27.7%).

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