LXXVI. — *Asymmetric Quaternary Arsonium Compounds and their Attempted Resolution.*

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THE fact that optical activity can be exhibited by substances containing no asymmetric atom other than one of quinquevalent nitrogen was first demonstrated by Pope and Peachey (Trans., 1899, **75**, 1127), who prepared *d*- and *l*-phenylbenzylmethylallyl-ammonium iodide and bromide; since that time a considerable number of other optically active substances, containing asymmetric nitrogen atoms, have been prepared by methods similar to those used by these workers. All attempts to prepare substituted ammonium salts of which the optical activity is associated with the presence of asymmetric quinquevalent atoms of other elements of group V of the periodic classification have, however, uniformly failed (Pope and Gibson, this vol., p. 735); as these attempts have

in general been made for the purpose of obtaining optically active substituted phosphonium salts, it seemed desirable to ascertain whether quaternary arsonium compounds containing an asymmetric quinquivalent arsenic atom could be obtained in optically active form.

The work on this subject described in the present paper, although unsuccessful in that it did not result in the association of optical activity with the presence of an asymmetric quinquivalent arsenic atom, led to the discovery of a number of novel reactions connected with the arsines, and is therefore now put forward.

It was confidently anticipated that on converting phenylbenzyl-methylallylarsonium iodide into the corresponding *d*-camphor- β -sulphonate or *d*- α -bromocamphor- π -sulphonate, and inoculating the supersaturated solution with crystals of *d*- or *l*-phenylbenzylmethylallylammonium *d*-camphor- β -sulphonate or *d*- α -bromocamphor- π -sulphonate, resolution would be effected; it was supposed that the arsonium and ammonium salts would prove isomorphous, and that the resolution would be assisted by the great facility with which the substituted ammonium camphorsulphonates crystallise. This anticipation was not realised, and in consequence it became of interest to study further the differences in behaviour thus indicated between arsenic and nitrogen compounds of corresponding compositions and constitutions.

The following points of difference have been found to exist. When phenyltrimethylammonium iodide is heated to 360° , it ultimately yields mesidine hydriodide; after heating phenyltrimethylarsonium iodide at 400° in a sealed tube for ten hours it may be recovered unchanged, despite the fact that this substance melts and decomposes at 248° in an open tube. The arsonium compound thus dissociates into phenyldimethylarsine and methyl iodide at 400° . When phenyltrimethylammonium hydroxide is heated it yields dimethylaniline and methyl alcohol; similarly, on distilling phenyltrimethylarsonium hydroxide in a current of steam, phenyldimethylarsine passes over. At the same time a minute quantity of a solid hygroscopic substance, non-volatile with steam and too small in amount for analysis, remains dissolved in the residual liquor. Phenyldimethylamine combines readily with diazonium salts, yielding azo-compounds; phenyldimethylarsine gives deeply coloured solutions with diazonium salts, but the reaction proceeds so slowly that the diazonium solution decomposes before sufficient of the azo-compound for examination is produced. With diazotised anthranilic acid, phenyldimethylarsine gives a red-coloured solution, which acts as an indicator in the same way as methyl-red, dimethyl-aminoazobenzene-*o*-carboxylic acid. When an amine containing a

halogen atom attached to the nitrogen atom is heated, the halogen atom enters the aromatic nucleus; phenylmethylbromoarsine, on the contrary, distils without change at 250° , and, even when heated with hydrogen bromide in acetic acid solution, affords no evidence of the migration of bromine into the nucleus.

After working for a short time with the substances now dealt with, unpleasant pathological effects are experienced. The vapours are apparently absorbed by the skin of the hands and face, and considerable nervous irritation is set up; ultimately, large blisters, resembling burns, are produced, and these disappear only after some weeks.

A considerable quantity of *phenylethyl-n-propylarsine*,

was prepared by the aid of the series of reactions represented by the following equations:

Of these reactions, numbers (1) and (2) were described by Michaelis, La Costa, and Reise (*Annalen*, 1880, **201**, 212; *Ber.*, 1882, **15**, 2876); in connexion therewith it may be remarked that light petroleum, boiling at 40 – 50° , may with advantage be substituted for ether, as used by Michaelis, and that in reaction (1) a much better yield of phenylarsine dichloride may be obtained by heating at 290 – 300° than at 250° .

Phenyldiethylarsine dibromide, $\text{C}_6\text{H}_5(\text{C}_2\text{H}_5)_2\text{AsBr}_2$, is obtained as a precipitated, white, crystalline mass on treating a light petroleum solution of bromine with a slight excess of phenyldiethylarsine; it melts and decomposes at 85° . The decomposition proceeds rapidly at 120° , torrents of ethyl bromide being evolved and phenylethylbromoarsine being produced:

$0\cdot2880$ gave $0\cdot2931$ AgBr. Br = $43\cdot3$.

$\text{C}_{10}\text{H}_{15}\text{Br}_2\text{As}$ requires Br = $43\cdot3$ per cent.

Phenylethylbromoarsine, $\text{C}_6\text{H}_5\cdot\text{As}(\text{C}_2\text{H}_5)\text{Br}$, is obtained in a state of purity by heating phenyldiethylarsine dibromide at 200° in a current of carbon dioxide; it forms a nearly colourless liquid, which decomposes, forming a black tar, when distilled under atmospheric pressure:

$0\cdot8036$ gave $0\cdot5642$ AgBr. Br = $30\cdot0$.

$\text{C}_8\text{H}_{10}\text{BrAs}$ requires Br = $30\cdot6$ per cent.

Phenylethylchloroarsine, $\text{C}_6\text{H}_5\cdot\text{As}(\text{C}_2\text{H}_5)\text{Cl}$, is obtained by heat-

ing phenyldiethylarsine dichloride at 160—180° in an open flask for twenty minutes. It is a colourless, highly refractive liquid, which boils with some decomposition at 249°:

0.6622 gave 0.4302 AgCl. Cl=16.1.

$C_8H_{10}ClAs$ requires Cl=16.4 per cent.

Owing to the difficulty of regulating the amount of chlorine required in the formation of phenyldiethylarsine dichloride, it is not easy to obtain this substance in a pure state.

Phenyldiethylarsine di-iodide, $C_6H_5(C_2H_5)_2AsI_2$, prepared by treating a petroleum solution of iodine with the requisite amount of phenyldiethylarsine, is a yellow, microcrystalline substance; it melts at 95°, and decomposes at 105°:

0.5525 gave 0.5460 AgI. I=54.5.

$C_{10}H_{15}I_2As$ requires I=54.7 per cent.

Phenylethyl-n-propylarsine, $C_6H_5(C_2H_5)As \cdot C_3H_7$, is prepared by the action of zinc propyl on phenylethylbromoarsine in ethereal solution in accordance with reaction (5); it is a colourless liquid, which boils at 245° without decomposition, and possesses the characteristic arsine odour. The tertiary arsine behaves as a very feeble base, and is not soluble in concentrated hydrochloric acid; it appears to oxidise but very slowly on exposure to the air.

Phenylbenzylmethyl-n-propylarsonium iodide,

is formed on heating a mixture of phenylethyl-n-propylarsine and benzyl iodide in molecular proportion at 40—50°; the reaction is complete in about two hours. The residue crystallises readily from ethyl acetate, and the salt is then obtained in small, colourless crystals, melting at 128°; the substance is readily soluble in alcohol, but insoluble in water:

0.5530 gave 0.2943 AgI. I=28.77.

$C_{13}H_{24}IAs$ requires I=28.75 per cent.

Phenylbenzylethyl-n-propylarsonium d-camphor-β-sulphonate,

is prepared by treating the foregoing compound in alcoholic solution with the requisite amount of silver *d*-camphor-β-sulphonate; after warming for some time reaction is complete, and the filtrate from the silver iodide yields, on evaporation, a viscous mass, which crystallises after some days. The salt is readily soluble in most organic solvents and in water, and is purified by fractional crystallisation from a mixture of acetone and light petroleum:

0.2179 gave 0.4907 CO₂ and 0.1501 H₂O. C=61.4; H=7.15.

$C_{28}H_{39}O_4SAs$ requires C=61.5; H=7.2 per cent.

No evidence of resolution was obtained during the fractional crystallisation of the salt, and the following determinations of rotatory power indicate that in aqueous solution the substance exhibits practically the molecular rotatory power of the acid ion:

0.5036 gram, made up to 30 c.c. with water at 15°, gave $\alpha + 0.81^\circ$ in a 4-dcm. tube; $[\alpha]_{\text{Hg green}} + 11.9^\circ$ and $[M]_{\text{Hg green}} + 64.9^\circ$.

On mixing concentrated aqueous solutions of the salt and potassium iodide, the corresponding iodide is precipitated and proved to be completely inactive in alcoholic solution.

Phenylethyl-n-propylallylarsonium bromide,

is prepared by the interaction of phenylethyl-n-propylarsine and allyl bromide; combination is complete in about twenty-four hours, and a solid, crystalline mass is obtained. The salt crystallises from acetone in large, colourless plates, melting at 86°, and is moderately soluble in water. The corresponding d- α -bromocamphor- π -sulphonate, $\text{C}_6\text{H}_5(\text{C}_3\text{H}_5)(\text{C}_2\text{H}_5)(\text{C}_8\text{H}_7)\text{As}\cdot\text{SO}_3\cdot\text{C}_{10}\text{H}_{14}\text{OBr}$, crystallises readily from dilute alcohol; it melts at 123°:

0.2051 gave 0.3446 CO_2 and 0.1130 H_2O . C=50.4; H=6.13.

$\text{C}_{24}\text{H}_{36}\text{BrI}_4\text{SAs}$ requires C=50.1; H=6.26 per cent.

The following determination of rotatory power was made with salt which had been recrystallised six times from acetone, and indicates that no resolution had been effected; the molecular rotatory power is practically that of the bromocamphorsulphonic acid ion in aqueous solution:

0.6252 gram, made up to 30 c.c. with water at 15°, gave $\alpha_{\text{Hg green}} + 5.00^\circ$; $[\alpha]_{\text{Hg green}} + 60^\circ$ and $[M]_{\text{Hg green}} + 345^\circ$.

Preparation of Phenylmethylallylarsine.

Since phenylbenzylmethylallylammonium iodide appears to be the most easily resolved of the known asymmetric quaternary ammonium compounds, it was decided, in view of the failure to resolve the arsonium salts above described, to attempt the preparation of the arsenic analogue of this ammonium derivative. For this purpose either phenylmethylallylarsine or phenylbenzylmethylarsine was required, and, as neither of these substances can be prepared by means of reactions (1) to (5), special methods of preparation had to be devised. As the result of a great deal of preliminary work, phenylmethylallylarsine was obtained by aid of the following series of reactions:

Phenyldimethylarsine was prepared by Michaelis and Link (*Annalen*, 1881, **207**, 205) by the action of zinc methyl on phenylarsenic dichloride; this method, however, gives a poor yield, mainly because of the difficulty of obtaining zinc methyl free from methyl iodide, the presence of which results in the formation of a quaternary arsonium compound. A much better yield (40 per cent. of theory) is obtained by the action of phenylarsenic dichloride diluted with ether on magnesium methyl iodide; the yield may be increased to 75 per cent. of the theoretical by diluting the phenylarsenic dichloride with light petroleum, boiling at 30—40°, instead of with ether. After treatment with water the phenyldimethylarsine is separated in the usual manner as a colourless oil, having the properties assigned to it by Michaelis and Link. On very cautiously treating its 5 per cent. solution in light petroleum with a 5 per cent. solution of bromine in the same solvent, and filtering off the petroleum, *phenyldimethylarsine dibromide*, $\text{C}_6\text{H}_5 \cdot \text{As}(\text{CH}_3)_2\text{Br}_2$, remains as a white, crystalline, slightly hygroscopic solid, which melts at 128° with violent decomposition. If, in this preparation, the phenyldimethylarsine is not constantly in excess, *phenyldimethylarsine tetrabromide*, $\text{C}_6\text{H}_5 \cdot \text{As}(\text{CH}_3)_2\text{Br}_4$, is produced. The latter compound, which is one of a class not previously described, is conveniently made by adding bromine (20 grams) to a light petroleum solution of phenyldimethylarsine (5 grams); a dark red oil separates, which crystallises on repeated washing with light petroleum. It forms dark red crystals, which melt at 61° without decomposition, and which, when heated at 160° for fifteen minutes, leave a residue of pure phenylarsenic dibromide; each molecule of the tetrabromide thus decomposes quantitatively, yielding one molecule of phenylarsenic dibromide and two molecules of methyl bromide. Analysis of the latter product indicated the presence of 50·7 per cent. of bromine, whilst the pure dibromide requires 51·2 per cent.:

0·5798 required 46·4 c.c. *N*/10- AgNO_3 . Br=64·0.

$\text{C}_8\text{H}_{11}\text{Br}_4\text{As}$ requires Br=63·75 per cent.

On heating phenyldimethylarsine dibromide at 180° until effervescence ceases and purifying the oily residue by repeated distillation, *phenylmethylbromoarsine*, $\text{C}_6\text{H}_5 \cdot \text{As}(\text{CH}_3)\text{Br}$, is obtained as a colourless liquid boiling at 250° without decomposition:

0·5492 gave 0·6067 AgBr . Br=47·0.

$\text{C}_7\text{H}_8\text{BrAs}$ requires Br=46·8 per cent.

The displacement of the bromine atom in phenylmethylbromoarsine by either the allyl or the benzyl radicle proved to be difficult; magnesium benzyl bromide acts on the bromoarsine, with formation of a mixture of products which could not be separated. Mercuric allyl iodide reacts violently with phenylmethylbromoarsine, yielding a gummy mass, which is not acted on by boiling dilute potassium hydroxide or by dilute acids.

Although allyl iodide in ethereal solution yields diallyl when treated with magnesium dust, it was found that the latter acts vigorously on a mixture of phenylmethylbromoarsine and allyl iodide in molecular proportion and in presence of ether, with the formation of very little diallyl; on working up the product in the usual way a liquid arsine of high boiling point was obtained. After repeated fractionation through a column in a current of hydrogen, impure *phenylmethylallylarsine*, $C_6H_5 \cdot As(CH_3) \cdot C_3H_5$, was obtained as a colourless liquid boiling at 192° ; further purification was impracticable, because slight decomposition occurs on distillation and because the arsine is too feebly basic to form stable salts.

On allowing a mixture of the impure arsine to remain for several days after mixing with the calculated quantity of benzyl iodide, a vitreous hygroscopic mass results, which can be caused to crystallise from acetone solution. After repeated crystallisation from this solvent, and finally from a mixture of acetone and alcohol, *phenylbenzylmethylallylarsonium iodide*,

is obtained in large, colourless crystals, melting at 100° . A very poor yield was obtained. The substance is insoluble in water, but dissolves readily in acetone, alcohol, or ethyl acetate:

0.3272 gave 0.1814 AgI. $I = 29.96$.

$C_{17}H_{23}IA$ s requires $I = 29.81$ per cent.

The above iodide reacts readily with the calculated quantity of silver *d*- α -bromocamphor- π -sulphonate under the usual conditions, and the resulting solution yields *phenylbenzylmethylallylarsonium d*- α -bromocamphor- π -sulphonate,

as a crystalline residue on evaporation. The salt crystallises from a mixture of alcohol and acetone in large, colourless prisms, melting at 189° :

0.2007 gave 0.3922 CO_2 and 0.1020 H_2O . $C = 53.4$; $H = 5.6$.

$C_{27}H_{34}O_4BrSAs$ requires $C = 53.2$; $H = 5.6$ per cent.

The following determination of rotatory power was made with salt which had been recrystallised four times from a mixture of alcohol and acetone:

0.5378 gram, made up to 30 c.c. with water at 15°, gave $\alpha_{\text{Hg green}} + 4.22^\circ$ in a 4-dcm. tube, whence $[\alpha]_{\text{Hg green}} + 58.8^\circ$ and $[M]_{\text{Hg green}} + 357^\circ$.

The value of $[M]_{\text{Hg green}}$ for the *d*-bromocamphorsulphonic ion is $+347^\circ$ (Pope and Read, *Trans.*, 1910, **97**, 2201), appreciably less than that just given; repeated crystallisation of the salt led to no change in the rotation constants, and it must consequently be concluded that no resolution had been effected. Further, the iodides precipitated from the solutions of the salt by addition of potassium iodide were all optically inactive. No separation could be caused by inoculating concentrated solutions with crystals of *d*- or *l*-phenylbenzylmethylallylammonium *d*- α -bromocamphor- π -sulphonate.

The salt of the asymmetric arsonium base with *d*-camphor- β -sulphonic acid was also prepared, but this could not be caused to crystallise, even by inoculating the syrupy solution with crystals of *d*- and *l*-phenylbenzylmethylallylammonium *d*-camphor- β -sulphonate.

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