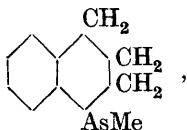


LIII.—*Experiments on the Production of Compounds containing Arsenic as a Centre of Optical Activity.*

By GEORGE JOSEPH BURROWS and EUSTACE EBENEZER TURNER.

MICHAELIS (*Annalen*, 1902, **321**, 159) and Winmill (T., 1912, **101**, 718) showed that certain derivatives of arsenic of the type As(abcd)X could not be obtained in an optically active condition. It appeared, however, to be necessary to attempt the resolution of different types of asymmetric arsenic compounds before concluding that arsenic is peculiar in not functioning as a centre of optical activity in any of its derivatives.

In view of the ease with which the resolution of kairolin oxide was accomplished by Meisenheimer (*Annalen*, 1911, **385**, 117), the authors prepared the compound :



the oxide of which would be the arsenic analogue of kairolin oxide, and, assuming the stereochemical relationships of the valencies of arsenic to be similar to those obtaining in the case of nitrogen, should be capable of resolution. The new arsine, for which the name *As*-methyltetrahydroarsinoline is suggested, is formed when aluminium chloride is allowed to act on  $\gamma$ -phenyl-*n*-propylmethylchloroarsine. Before this ring-closure was attempted, experiments were conducted on the action of aluminium chloride on mixtures of benzene with various chloroarsines, and it was found that, although as stated by Michaelis and others (*Annalen*, 1880, **201**, 184, etc.) the Friedel-Crafts' reaction was not generally applicable in the preparation of arsenic compounds, monochloroarsines were readily converted into tertiary arsines by the reaction in question, phenylmethylchloroarsine, for example, being readily converted into diphenylmethylarsine in the presence of benzene. An interesting case of selective action was observed in this connexion, a mixture of  $\gamma$ -phenyl-*n*-propylmethylchloroarsine and benzene giving no phenylpropylphenylmethylarsine, but only *As*-methyltetrahydroarsinoline.

Owing to lack of material the arsinoiline could not be prepared in sufficient quantity to allow an investigation of the oxide and of the hydroxyarsinolinium compounds with active acids.

As a second series, an arsenic analogue of the asymmetric amine-

and phosphine-oxides was studied. The majority of the asymmetric arsine oxides are liquids, and in view of the uncertainty attached to such compounds an endeavour was made to obtain a solid oxide; after many experiments a solid arsine was finally obtained (phenyl- $\alpha$ -naphthylmethylarsine), and from this a well-defined oxide was prepared. It combined readily with *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonic acid, but the bromocamphorsulphonate obtained in this way gave no indication of being separable into two substances of different rotatory power.

Attention was finally directed to the study of substances of the simple, asymmetric arsonium type. A large number of such compounds were prepared, but two series only were suitable to the investigation.

The first series, derived from the homopiperonylphenyl- $\alpha$ -naphthylmethylarsonium ion, gave indefinite results. The bromocamphorsulphonate could not be obtained free from alcohol of crystallisation, and although on fractionation definite indications of resolution were observed, the authors hesitated to regard this as sufficient evidence for the existence of optically active arsenic derivatives, particularly in view, on the one hand, of the difficulty with which the crystallisation of the bromocamphorsulphonate was attended, and, on the other, of the impossibility of obtaining in the active condition an arsenic compound free from camphor.

The second series, derived from the phenyl- $\alpha$ -naphthylbenzylmethylarsonium ion, gave definite results, one recrystallisation of the bromocamphorsulphonate affording a substance the molecular rotation of which,  $[M]_D + 300^\circ$ , differed by some twenty units from the rotation of the bromocamphorsulphonic ion ( $+ 278^\circ$ ); further recrystallisation produced no effect on the molecular rotation. This substance, on treatment with potassium iodide or bromide, was converted into the haloid salt, which had a definite, positive rotation. Racemisation occurred with such rapidity, however, that on no occasion was a molecular rotation of more than  $12^\circ$  (iodide) obtained. Racemisation would appear to occur as the result of the tendency of quaternary arsonium salts to dissociate readily in solution; thus, the iodide of the series in question dissociated in chloroform solution, at least partly, to give benzyl iodide and phenyl- $\alpha$ -naphthylmethylarsine.

The tendency of derivatives of quinquevalent arsenic to break down in solution into derivatives of trivalent arsenic would appear to be more pronounced than the tendency of similar derivatives of nitrogen, and besides affording a possible explanation of the failure of previous workers to obtain optically active derivatives of arsenic, would account for other anomalies observed in the

study of the organic derivatives of this element, such as the properties of the additive compounds described in a previous paper (Burrows and Turner, T., 1920, **117**, 1373), the intramolecular change referred to in the experimental portion of this paper in connexion with the heterocyclic derivative, and also the crystallisation, from solution, of mixtures of quaternary salts as a result of the interaction of an arsine and an alkyl iodide.

#### EXPERIMENTAL.

##### *γ-Phenylpropyl Alcohol and γ-Bromopropylbenzene.*

*γ*-Phenylpropyl alcohol was prepared by reducing ethyl *β*-phenylpropionate with sodium and alcohol by Bouveault's method (*Compt. rend.*, 1903, **136**, 1676). The use of absolute alcohol was necessary, as the presence of water in small quantity caused the formation of insoluble sodium salts, which coated the sodium and prevented its dissolution. A solution of ethyl *β*-phenylpropionate (23·5 c.c.) in 125 c.c. of absolute alcohol was slowly added, under reflux, to a vigorously shaken mixture of small pieces of sodium (19 grams) and broken glass, the last traces of sodium were destroyed by the addition of 50 c.c. of absolute alcohol, and the solution was carefully decomposed with water. The products of several such reductions were united, acidified with hydrochloric acid, neutralised with sodium carbonate, freed from alcohol by distillation and extracted with ether. From the extract phenylpropyl alcohol, b. p. 124—125°/16 mm., was obtained in amount corresponding with a 65 per cent. conversion, whilst by acidifying the extracted solution and again extracting with ether, *β*-phenylpropionic acid was recovered, the total loss of material amounting to less than 10 per cent. of the initial quantity.

The bromo-compound was readily prepared by Rupe and Bürgin's method (*Ber.*, 1910, **43**, 178).

##### *γ-Phenylpropyldimethylarsine.*

(a) *Dimethyliodoarsine.*—The following method of preparation is simpler than that described previously (Burrows and Turner, *loc. cit.*).

Arsenious oxide (320 grams), methyl iodide (206 c.c.), and sodium hydroxide (388 grams) were dissolved together in aqueous alcohol. After about twenty hours, the alcohol was removed by distillation and the residue acidified with hydrochloric acid and saturated with sulphur dioxide. The methyldi-iodoarsine that separated (835 grams) was removed, dissolved in 1700 c.c. of alcohol, and

treated with a solution of 408 grams of sodium hydroxide in 600 c.c. of water and with 170 c.c. of methyl iodide. On the next day the alcohol was removed by distillation, and the residue acidified with hydrochloric acid and saturated with sulphur dioxide. The yield of dimethyliodoarsine (435 grams) was 58 per cent. of that theoretically obtainable from the arsenious oxide used.

(b) *γ-Phenylpropyldimethylarsine*.—Dimethyliodoarsine (35 grams) dissolved in 100 c.c. of benzene, was slowly added, with shaking, to a Grignard reagent prepared from 40 grams of *γ*-bromopropylbenzene, 5 grams of magnesium, and 100 c.c. of ether, the mixture finally being heated in warm water for an hour. The formation of an additive compound in considerable quantity necessitated the extraction of the ethereal solution (obtained in the usual manner from the reaction product) with an aqueous solution of sodium hydroxide. The arsine was finally obtained as a colourless, highly refractive liquid, b. p. 133°/14 mm. (Found: As = 32·9.  $C_{11}H_{17}As$  requires As = 33·5 per cent.). The yield was 65 per cent. of the theoretical.

The *methiodide* was formed readily, and crystallised from water in colourless needles melting at 144° (Found: I = 34·3.  $C_{12}H_{20}IA_s$  requires I = 34·7 per cent.).

An *additive* compound,  $C_{11}H_{17}As, Me_2AsI$ , was formed when the arsine (1 mol.) was mixed with dimethyliodoarsine (1 mol.). It crystallised from ether, methyl alcohol, or even from concentrated hydrochloric acid, and formed colourless prisms melting at 78–81°. It was completely dissociated into its components in benzene solution (Found: I = 27·8; M. [by the cryoscopic method in benzene] 222, 224.  $C_{13}H_{23}IA_s_2$  requires I = 27·9 per cent.; M. = 456).

*γ*-Phenylpropyldimethylarsine is the only one of the twelve or more arsines examined that forms an additive compound with dimethyliodoarsine.

#### *Phenylmethyliodoarsine and Phenylmethylchloroarsine.*

The method previously described for the preparation of these compounds (Burrows and Turner, *loc. cit.*) has been greatly simplified. A solution containing 365 grams of phenyldichloroarsine, 1200 c.c. of alcohol, 280 grams of sodium hydroxide and 260 grams of methyl iodide, after remaining for one day, was neutralised with hydrochloric acid. The sodium chloride was removed by filtration and the alcohol by distillation, the phenylmethyliodoarsine, which separated to a considerable extent at this stage, was redissolved by adding water, and the solution saturated with sulphur dioxide after the addition of hydrochloric acid. In this way 435 grams

of phenylmethyliodoarsine were obtained. The corresponding chloro-compound was prepared from it by the method previously described.

*Conversion of Phenylmethylchloroarsine into  
Diphenylmethylarsine.*

A mixture of 15 grams of the chloro-compound, 60 grams of benzene, and 10 grams of aluminium chloride was gently heated for two hours. Hydrogen chloride was evolved immediately. The product was decomposed with ice and dilute hydrochloric acid, and 7 grams of pure diphenylmethylarsine (identified as the methiodide) were obtained.

*$\gamma$ -Phenylpropylmethylchloro- and -bromo-arsines.*

$\gamma$ -Phenylpropyldimethylarsine (45 grams) was treated in carbon tetrachloride solution with chlorine (1 mol.) dissolved in the same solvent. The pale yellow solution obtained in this way was evaporated and the residue heated at 160—180°, when it decomposed readily with the evolution of methyl chloride, volatile chloroarsines and  $\gamma$ -chloropropylbenzene also being formed in small quantities. The required chloroarsine was obtained (22 grams) as a colourless liquid, b. p. 164—167°/14 mm., when the final residue was distilled under diminished pressure. It could not be obtained free from traces of the original arsine which had been formed by the dissociation of the dichloride into its parent substances (Found: Cl = 13·5.  $C_{10}H_{14}ClAs$  requires Cl = 14·5 per cent.).

The corresponding bromo-compound was obtained in a similar manner. The dibromide of the original arsine decomposed readily at 170° and  $\gamma$ -phenylpropylmethylbromoarsine, a colourless liquid, b. p. 177—180°/16 mm., was produced, but it contained traces of dibromoarsine (Found: Br = 28·6.  $C_{10}H_{14}BrAs$  requires Br = 27·7 per cent.).

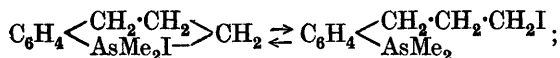
*As-Methyltetrahydroarsinoline.*

1. *Preparation in Carbon Disulphide Solution.* (a) *From  $\gamma$ -Phenylpropylmethylchloroarsine.*—A mixture of the chloroarsine (5 grams), carbon disulphide, and aluminium chloride (2·7 grams) was gently boiled for three hours, when hydrogen chloride ceased to be evolved. The product was decomposed with ice, and the mixture, after being acidified, was extracted with carbon tetrachloride. From the extract, by distillation under diminished pressure, 2 grams of *As-methyltetrahydroarsinoline*, a colourless liquid, b. p. 140°/14 mm., were obtained (Found: C = 56·6; H = 5·8; M. [by the cryoscopic method in benzene] 205, 206.  $C_{10}H_{13}As$  requires C = 57·7; H = 5·8

per cent.;  $M = 208$ ). The difficulty of separating arsines from chloroarsines was again encountered here, and although the boiling point of the substance analysed was quite constant, the preparation of the pure arsinoline from the small quantity of material was impossible. Its constitution, however, is proved by the analysis of its derivatives and by the value of the molecular weight.

As-*Methyltetrahydroarsinoline* is a highly refractive liquid having an odour faintly suggestive of quinoline. It is slowly oxidised in the air and dissolves in concentrated sulphuric acid to give a colourless solution, from which water precipitates the unchanged arsine.

The *methiodide* is readily formed, and crystallises from alcohol or water in colourless prisms melting at  $235^\circ$  (Found:  $I = 36.1$ .  $C_{11}H_{16}IAs$  requires  $I = 36.3$  per cent.). A hot, alcoholic solution has a yellow colour, which disappears when the solution is cooled. This property is probably due to an intramolecular change,



a rapid estimation of the iodine content with a dilute, alcoholic solution of silver nitrate gave a value 7 per cent. lower than that obtained by the usual analytical method.

The *platinichloride*, obtained in the usual manner, is a yellow, microcrystalline powder melting at  $170^\circ$  (Found:  $Pt = 23.9$ .  $2C_{10}H_{13}As, H_2PtCl_6$  requires  $Pt = 23.7$  per cent.).

The arsinoline forms other well-defined salts, the *picrate* and the *picrolonate* being yellow, crystalline solids.

(b) *From  $\gamma$ -Phenylpropylmethylbromoarsine*.—The bromoarsine (21 grams) was treated in the same manner as the chloro-compound, and gave rise to 10 grams of the arsinoline.

(2) *In Benzene Solution*.—The chloro-arsine (10 grams), when gently heated for three hours with 70 c.c. of benzene in presence of 6.5 grams of aluminium chloride, gave rise to 6 grams of the arsinoline, no phenyl- $\gamma$ -phenylpropylmethylarsine (see below) being formed.

#### *Phenyl- $\gamma$ -phenylpropylmethylarsine.*

Phenylmethyliodoarsine (88.3 grams) was slowly added to a Grignard reagent prepared from 63 grams of  $\gamma$ -bromopropylbenzene, 10 grams of magnesium, and 300 c.c. of ether. After the usual procedure the final ethereal extract was washed with an aqueous solution of sodium hydroxide to remove the unchanged iodoarsine. The *phenyl- $\gamma$ -phenylpropylmethylarsine* (60 grams) obtained in this way was a colourless, highly refractive liquid, boiling at  $208^\circ/17$  mm. (Found:  $As = 26.1$ .  $C_{16}H_{19}As$  requires  $As = 26.2$  per cent.).

The *methiodide* was formed readily, and crystallised from water

in colourless rhombohedra melting at  $102^{\circ}$  (Found : I = 29.6.  $C_{17}H_{22}IAs$  requires I = 29.7 per cent.).

The *dichloride* was readily formed, but on heating gave a mixture of products, which was not further investigated.

*Phenyl- $\alpha$ -naphthylmethylarsine.*

This was prepared by the usual procedure. From 117 grams of phenylmethyliodoarsine, 94 grams of  $\alpha$ -bromonaphthalene and 14 grams of magnesium in ethereal solution, 102 grams of *phenyl- $\alpha$ -naphthylmethylarsine*, a colourless, crystalline solid, m. p.  $58^{\circ}$ , b. p.  $236-238^{\circ}/17$  mm., were obtained (Found : As = 25.7.  $C_{17}H_{15}As$  requires As = 25.5 per cent.). The arsine was readily soluble in ether and crystallised best from alcohol.

The *methiodide* was readily formed on the water-bath and separated from concentrated alcoholic solution in colourless plates melting at  $175^{\circ}$  (Found : I = 28.9.  $C_{18}H_{18}IAs$  requires I = 29.1 per cent.).

*Phenyl- $\alpha$ -naphthylmethylarsine Oxide.*

The preceding arsine was dissolved in chloroform and bromine (1 mol.; dissolved in chloroform) added, the mixture being well cooled to prevent bromination. The resulting solution was shaken with a slight excess of an aqueous solution of sodium hydroxide, the mixture separated, the chloroform layer washed with water, and then dried and evaporated. After the oxide had once been obtained crystalline, the residue in subsequent experiments became solid at this stage, and after being heated at  $120^{\circ}$  for a short time (to remove traces of the *dihydroxide*) yielded the oxide in an almost pure state. The latter was crystallised from toluene and formed colourless, well-defined prisms melting at  $175^{\circ}$  (Found : As = 23.7.  $C_{17}H_{15}OAs$  requires As = 24.2 per cent.).

*Hydroxyphenyl- $\alpha$ -naphthylmethylarsonium d- $\alpha$ -Bromocamphor- $\pi$ -sulphonate.*

The preceding compound, although almost insoluble in ethyl acetate, dissolved immediately in a solution of *d- $\alpha$ -bromocamphor- $\pi$ -sulphonic acid* (1 mol.) in this solvent, with the evolution of heat. The *bromocamphorsulphonate*, m. p.  $161^{\circ}$ , being insoluble in cold ethyl acetate, crystallised from the solution on cooling (Found : C = 51.9; H = 5.1.  $C_{27}H_{30}O_5BrSAs$  requires C = 52.2; H = 4.9 per cent.). Repeated attempts were made to separate this substance into two diastereoisomerides, but the differences of molecular rotation observed with successive crops of crystals, although



definite, were small and could not be appreciably increased by further fractionation.

A solution of the original bromocamphorsulphonate (0.4963 gram) in 10 c.c. of alcohol, diluted to 50 c.c. with water, gave in a 2-dem. tube  $\alpha_D + 0.89^\circ$ ;  $[M]_D + 278^\circ$ . (Silver *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate under similar conditions gave  $[M]_D + 277^\circ$ ). When the bromocamphorsulphonate was crystallised from alcohol, or from a mixture of alcohol and ethyl acetate, the first crop of crystals (in several preparations) invariably gave a rotation of  $+286^\circ$  or slightly higher; for example, a solution containing 0.5210 gram in 50 c.c. of 20 per cent. alcohol gave in a 2-dem. tube,  $\alpha_D + 0.96^\circ$ ;  $[M]_D + 286^\circ$  (Found: C = 52.2; H = 4.9 per cent.).

The results, however, were regarded as insufficient evidence upon which to base the assumption that arsenic was functioning as a centre of optical activity in this compound.

#### *Methylethyliodoarsine.*

Ethyldi-iodoarsine (250 grams) was dissolved in a solution of 122 grams of sodium hydroxide in 200 c.c. of water and 600 c.c. of alcohol, and the mixture treated with 75 c.c. of methyl iodide under reflux. Methylation was complete after a few hours, and the solution, having been neutralised and freed from alcohol, was acidified with hydrochloric acid and reduced with sulphur dioxide. The oil that separated was collected, dried, and distilled under diminished pressure, when 138 grams of methylethyliodoarsine, a yellow, oily liquid, b. p.  $65^\circ/14$  mm., were obtained. It boiled with slight decomposition under atmospheric pressure, spontaneous ignition occurring occasionally (Found: I = 51.2.  $C_3H_8IA_2$  requires I = 51.6 per cent.).

#### *Phenylmethylethylarsine and Derived Asymmetric Quaternary Compounds.*

This arsine was obtained either from the preceding iodo-compound and magnesium phenyl bromide, or from phenylmethyliodoarsine and magnesium ethyl bromide (Burrows and Turner, *loc. cit.*). It combined readily with allyl bromide, homopiperonyl bromide,  $\omega$ -bromoacetophenone, bromoacetic acid, and benzyl bromide; combination with the last-mentioned substance occurred violently with the formation of a glassy material, which was probably a mixture and could not be crystallised. The same difficulty was encountered with the other compounds.



*Phenyl- $\alpha$ -naphthylmethylarsonium Bromide.*

Phenyl- $\alpha$ -naphthylmethylarsine combined readily with allyl bromide to give a colourless, crystalline compound melting and decomposing at 140° (Found: Br = 18·8.  $C_{20}H_{20}BrAs$  requires Br = 19·3 per cent.). It proved unsuitable, however, for conversion into a bromocamphorsulphonate.

*Phenacylphenyl- $\alpha$ -naphthylmethylarsonium Bromide.*

When phenyl- $\alpha$ -naphthylmethylarsine and  $\omega$ -bromoacetophenone were warmed together in molecular proportions, a glassy substance was produced, which, in contact with warm alcohol, slowly changed into a bulky, white, crystalline solid melting at 189° (Found: Br = 16·1.  $C_{25}H_{22}OBrAs$  requires Br = 16·2 per cent.). It dissolved sparingly in cold alcohol, readily in hot alcohol, and was insoluble in acetone.

The corresponding bromocamphorsulphonate was obtained as a glassy mass which resisted repeated attempts at crystallisation.

*Homopiperonylphenyl- $\alpha$ -naphthylmethylarsonium d- $\alpha$ -Bromocamphor- $\pi$ -sulphonate.*

Homopiperonyl bromide was prepared by treating homopiperonyl alcohol with twice its weight of hydrobromic acid (saturated at 0°), the use of a larger excess of the acid (Robinson and Robinson, T., 1914, 105, 1463) being unnecessary.

The bromide combined readily and quantitatively when warmed with a molecular quantity of phenyl- $\alpha$ -naphthylmethylarsine. The *arsonium bromide* was crystallised from alcohol and formed colourless plates melting at 174—175° (Found: Br = 15·7.  $C_{25}H_{22}O_2BrAs$  requires Br = 15·7 per cent.).

The bromide was heated in alcoholic solution with the calculated quantity of silver *d- $\alpha$ -bromocamphor- $\pi$ -sulphonate*, the silver bromide removed, and the filtrate evaporated under diminished pressure. After several days, a crystalline mass of stout needles was obtained. It was, however, impossible to obtain a really suitable solvent for the purpose of fractional crystallisation. The most suitable one was absolute alcohol; very concentrated solutions in this solvent, however, only very slowly deposited crystals, which, moreover, contained alcohol of crystallisation (Found: C = 56·3; H = 5·5.  $C_{35}H_{36}O_6BrSAs, C_2H_6O$  requires C = 56·6; H = 5·4 per cent.).

Nevertheless, an attempt was made to separate the substance into two forms by fractional crystallisation from alcohol. The several fractions gave values of  $[M]_D$  varying from +278° to +300°. On recrystallising a fraction of low rotation, the

molecular rotation could not be increased. Furthermore, it was impossible to obtain the arsonium bromide free from the bromocamphorsulphonate. On mixing an aqueous solution of potassium bromide with a solution of the bromocamphorsulphonate in acetone, an oily precipitate separated, which became crystalline when rubbed, but was contaminated with the bromocamphorsulphonate even after thorough washing.

*Phenyl- $\alpha$ -naphthylbenzylmethylarsonium Bromide and d- $\alpha$ -Bromocamphor- $\pi$ -sulphonate.*

Phenyl- $\alpha$ -naphthylmethylarsine and benzyl bromide combined readily on the water-bath to give the *arsonium bromide*, colourless prisms (from alcohol), m. p.  $185^{\circ}$  (Found: Br = 17.1.  $C_{24}H_{22}BrAs$  requires Br = 17.2 per cent.). The bromide was readily soluble in hot alcohol, but dissolved sparingly in cold alcohol, from which it crystallised slowly. Although it was insoluble in water, it dissolved readily in cold dilute alcohol, a fact which can only be explained from the ionic point of view.

When the bromide was treated with the calculated quantity of silver *d- $\alpha$ -bromocamphor- $\pi$ -sulphonate* in the manner described above, the *bromocamphorsulphonate* was obtained as a glassy mass which became crystalline after remaining for a few days in contact with alcohol and ethyl acetate in a dry atmosphere. It was then found to crystallise from a mixture of alcohol and ethyl acetate, from acetone, or from a mixture of acetone and ether. This bromocamphorsulphonate, unlike the homopiperonyl derivative described above, separated rapidly from its solutions, and the various crops of crystals were analytically identical (Found: C = 58.4; H = 5.3.  $C_{34}H_{36}O_4BrSAs$  requires C = 58.7; H = 5.2 per cent.). The original substance formed colourless prisms melting at  $187^{\circ}$  and was more soluble in a mixture of acetone (or alcohol) and water than in acetone (or alcohol), although it was almost insoluble in water.

The molecular rotation was determined in a 20 per cent. solution of acetone at  $20^{\circ}$ , parallel determinations being made with silver *d- $\alpha$ -bromocamphor- $\pi$ -sulphonate*. A solution containing 0.4952 gram in 50 c.c. gave, in a 2-dcm. tube,  $\alpha_D + 0.80^{\circ}$ ;  $[M]_D + 281^{\circ}$  (0.5112 gram of the silver salt gave  $[M]_D + 278^{\circ}$ ). The bromocamphorsulphonate was then recrystallised once from a mixture of acetone and ether: 0.4984 gram, under the conditions stated above, gave  $\alpha_D + 0.86^{\circ}$ ;  $[M]_D + 300^{\circ}$ . The product obtained in this way, representing less than one-third of the original bromocamphorsulphonate, was then recrystallised four times from the same medium, but suffered no change of rotatory power.

Fresh samples of the bromocamphorsulphonate were prepared from the bromide on several occasions, and the same results were obtained after crystallisation. The authors regard this as evidence that the arsenic atom is capable of acting as a centre of optical activity, the arsonium ion in the most active of the bromocamphorsulphonate solutions having  $[M]_D + 20^\circ$ . Attempts to obtain evidence of the existence of the *l*-arsonium ion were unsuccessful.

*d*-Phenyl- $\alpha$ -naphthylbenzylmethylarsonium *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonate has the same melting point as the *dl*-isomeride, which apparently is a pseudo-racemic mixture. When treated in aqueous-acetone solution with an aqueous solution of potassium iodide, the *arsonium iodide* separated in colourless needles melting at 186—187° (Found: I = 24.6.  $C_{24}H_{22}IA_3$  requires I = 24.8 per cent.). The *d*-iodide is soluble in cold chloroform or in a cold mixture of alcohol and water, also in warm alcohol or warm acetone; solutions in the last two solvents deposit crystals of the inactive iodide after cooling for some time. Solutions of the *d*-iodide in these solvents were examined polarimetrically and in every case a positive rotation was observed, which, although small, was quite definite; the highest molecular rotation obtained was given by a solution prepared by dissolving 1.0258 grams in a warm mixture of 25 c.c. of acetone and 15 c.c. of alcohol, which, after cooling in the absence of nuclei, gave in a 2-dcm. tube,  $\alpha_D + 0.10^\circ$ ;  $[M]_D + 12^\circ$ . When the *d*-iodide was recrystallised from hot acetone or alcohol, the product was inactive and melted at 183—184°. The melting points of the active and the inactive iodides varied over one or two degrees according to the rate of heating. The observed rotations of solutions in chloroform or in aqueous-alcoholic mixtures were of the order  $[M]_D + 5^\circ$ .

The *bromide*, prepared in a similar manner as the iodide, gave results of the same type. The *d*-bromide was obtained in colourless crystals melting at 187—188°, but racemisation in solution was rapid and the highest molecular rotation observed was  $[M]_D + 5^\circ$ .

#### *Formation and Dissociation of Quaternary Arsonium Compounds.*

The melting point of the methiodide derived from phenyldiethylarsine has been recorded as 75—77° (Burrows and Turner, *loc. cit.*), and 122° (Michaelis, *Annalen*, 1902, **320**, 296). Methyl iodide and phenyldiethylarsine (the latter prepared from phenyldichloroarsine by the action of either zinc ethyl or magnesium ethyl bromide) have now been allowed to interact under a variety of conditions; the product had a melting point within a few degrees of that previously recorded by us. Products having almost the same

melting point have also repeatedly been obtained from ethyl iodide and phenylmethylethylarsine (prepared from phenylmethyliodoarsine and also from methylethylidoarsine). The analysis of each of these products agrees approximately with the formula  $C_{11}H_{18}IAs$ , and it is possible that our products, none of which has a well-defined melting point, are mixtures of one molecular proportion of phenyltrimethylarsonium iodide with two molecular proportions of phenyltriethylarsonium iodide. We have been unable to isolate under any conditions a compound melting at  $122^\circ$ .

Similarly, when phenyldimethylarsine was allowed to react with ethyl iodide, the product varied with the conditions (solvent, temperature, etc.) employed. Thus, on allowing a mixture of the arsine and ethyl iodide in ethereal solution to remain overnight, a very small crop of crystals, m. p.  $190^\circ$ , was deposited. The main product obtained by warming the filtrate on the water-bath, melted at  $142^\circ$ , and was identical with the methiodide of phenylmethylethylarsine (described previously). The product melting at  $190^\circ$  gave  $I = 38.6$ .  $PhMe_2EtAsI$  requires  $I = 37.6$ ,  $PhMe_3AsI$  requires  $I = 39.2$  per cent. This result is extraordinary, since it involves the replacement of an ethyl group by a methyl group in the presence of an excess of ethyl iodide, and the result can only be explained by assuming that the first product is phenyldimethylarsine ethiodide, which dissociates to form phenylmethylethylarsine and methyl iodide, the latter then combining with unchanged phenyldimethylarsine. On the other hand, the product from phenylmethylethylarsine and methyl iodide always melted at  $142^\circ$ .

In view of these results it seems improbable that quaternary arsonium compounds containing two similar radicles can exist in more than one form. Repeated attempts have been made to throw light upon this question, and each result necessitates the same conclusion. It has been found, for example, that identical products are obtained from  $\alpha$ -naphthylmethylethylarsine and methyl iodide and from  $\alpha$ -naphthyldimethylarsine and ethyl iodide, and also from  $\gamma$ -iodopropylbenzene and phenyldimethylarsine and from  $\gamma$ -phenylpropyldimethylarsine and methyl iodide. Again, although phenyl- $\alpha$ -naphthylmethylarsine as a rule behaves normally with alkyl haloids, it gives a mixture of products when warmed with ethyl iodide. The results, in fact, recall the work of Pope (T.. 1901, **79**, 831; 1912, **101**, 529), and others on quaternary ammonium salts, except in so far as the latter are apparently far less easily dissociated than the analogous derivatives of arsenic.

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