146. *The Synthetic Application of* o-β-*Bromoethylbenzyl Bromide. Part III. The Preparation and Optical Resolution of* 2-*Phenyl*-2-p-*chlorophenacyl*-1 : 2 : 3 : 4-*tetrahydro*isoarsinolinium *Bromide.*

By Frederick G. Holliman and Frederick G. Mann.

2-Phenyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinoline readily combines with *p*-chlorophenacyl bromide to give the above *iso*arsinolinium bromide, a salt of considerable stability, which has been resolved into optically active forms *via* the bromocamphorsulphonate. The corresponding *d*- and *l*-*iso*arsinolinium picrates have thus been obtained having $[M]_D$ + 457° and − 450°, and the corresponding *l*-iodide having $[M]_D$ − 354°; both salts are optically stable in chloroform solution at room temperature. These are the first arsonium salts to be obtained in optically stable forms, and the correlation of their optical and chemical stability provides strong evidence that the optical instability previously recorded for dissymmetric arsonium salts has been due to the formation of a " dissociation-equilibrium " in solution. The properties of other dissymmetric 4-covalent arsenic compounds are discussed on this basis.

The resolution into optically active forms of phenylbenzylmethylallylammonium iodide by Pope and Peachey (J., 1899, **75**, 1127), and the subsequent resolution of several other quaternary ammonium salts of this type, leave little doubt that similar quaternary phosphonium and arsonium salts should also be susceptible to optical resolution, for it is exceedingly unlikely on theoretical grounds that the phosphorus and arsenic compounds possess a configuration essentially different from that of similar nitrogen derivatives.

Nevertheless, it is a striking fact that no phosphorus compound of type [abcdP]X, where a, b, c, d, represent alkyl or aryl groups and X a univalent acid radical, has yet been resolved. Furthermore, although several attempts have been made to resolve a similar arsenic compound [abcdAs]X, only two have been successful, and in both these cases, the arsenic salt possessed only a very small and fleeting optical rotation. For instance, Michaelis (*Annalen*, 1902, **321**, 159) failed to resolve phenyl-*p*-tolylmethylethylarsonium iodide, and Winmill (J., 1912, **101**, 720) also failed with phenylbenzylmethylallylarsonium iodide and other similar salts. Burrows

and Turner (J., 1921, **119**, 426) prepared phenyl-α-naphthylbenzylmethylarsonium bromide, converted it into the *d*-bromocamphorsulphonate, and separated the latter by recrystallisation into two fractions having $[M]_D$ + 281° and + 300° severally. The latter fraction was then converted into the arsonium iodide, which however possessed a fleeting rotation, the highest value measured being $[M]_D$ + 12°. Kamai (*Ber.*, 1933, **66**, 1779; *J. Gen. Chem. Russia*, 1934, **4**, 184) prepared *p*-tolylbenzylethyl-*n*-propylarsonium iodide, converted it into the *d*-bromocamphorsulphonate, and separated the latter similarly into three fractions having $[M]_D$ + 318°, + 291°, and + 285°. The first was converted into an (unanalysed) iodide having $[M]_D$ + 45°, which rapidly racemised in solution; the other two fractions gave inactive iodides. Recently, this author (*ibid.*, 1942, **12**, 104) recorded his failure to obtain any evidence of resolution by the recrystallisation of *p*-tolyl-α-naphthylbenzylethylarsonium *d*-bromocamphorsulphonate and of its β-naphthyl isomer.

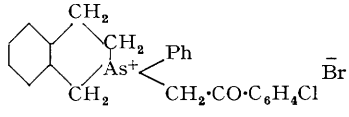
The probable cause of this striking difference in the ease of resolution of dissymmetric quaternary salts of nitrogen compared with those of phosphorus and arsenic is not difficult to formulate. It is known that the optically active quaternary ammonium sulphates and nitrates possess considerable optical stability and are difficult to racemise; the corresponding halides, particularly the iodides, however, racemise much more readily. This racemisation of the iodides is largely determined by the solvent employed: in aqueous solution, the racemisation is slow, but in chloroform solution, even at room temperature, it is comparatively rapid. It was first suggested by Pope and Harvey (J., 1901, **79**, 831) that the racemisation of *d*-phenylbenzylmethylallylammonium iodide in cold chloroform solution was due to the establishment of an equilibrium between the salt and its dissociation products:

$$[N(C_7H_7)(C_6H_5)(C_3H_5)(CH_3)]I \rightleftarrows N(C_6H_5)(C_3H_5)(CH_3) + C_7H_7I$$

This possibility was investigated in detail by other workers (see in particular Wedekind and co-workers, *Ber.*, 1902, **35**, 760; *Z. Elektrochem.*, 1906, **12**, 330; *Ber.*, 1908, **41**, 1029, 2659; von Halban, *Z. Elektrochem.*, 1907, **13**, 57; *Ber.*, 1908, **41**, 2417), and the existence of this dissociation equilibrium conclusively proved. This explains the optical stability of the quaternary ammonium sulphates and nitrates, which of course could not readily undergo a similar dissociation. Burrows and Turner (*loc. cit.*) obtained strong evidence that quaternary arsonium iodides also give rise to a dissociation equilibrium, [abcdAs]I ⇄ abcAs + dI, and attributed the difficulty of obtaining optically stable halide salts to the ready formation of this equilibrium. [It is noteworthy that most dissymmetric quaternary ammonium, phosphonium, and arsonium salts whose resolution has been attempted have for synthetic reasons contained a benzyl radical, which of course lends itself particularly readily to the above dissociation, with formation of benzyl iodide (cf. Snyder and Speck, *J. Amer. Chem. Soc.*, 1939, **61**, 669, 2895).]

Some indirect evidence in favour of this dissociation theory of optical instability as applied to arsonium salts was obtained by Chatt and Mann (J., 1939, 610), who separated ethylene-αβ-bis(phenylmethyl-*n*-butylarsonium picrate) (I) by fractional crystallisation into two isomeric forms, one of which must have been the *meso* and the other the racemic form. The isomerides underwent no interconversion even in boiling alcoholic

(I.) $CH_2(\overset{+}{A}sPhMeBu)$ | $CH_2(\overset{+}{A}sPhMeBu)$ $\{O{\cdot}C_6H_2(NO_2)_3^-\}_2$

(II.) 

solution. Such an interconversion, had it occurred, would clearly have involved a change of configuration of one of the asymmetric arsenic atoms in the molecule; this in turn, on the dissociation theory, would have involved formation of a di-tertiary arsine and of an alkyl picryl ether, which is clearly exceedingly unlikely to occur.

The validity of the dissociation theory of the optical instability of arsonium salts could be tested by the attempted resolution of a salt [abcdAs]X, in which a, b, c, d were different *aryl* radicals, and in which dissociation could hardly occur. The preparation of such a salt is possible by Chatt and Mann's aluminium chloride reaction (J., 1940, 1192; 1942, 666) and experiments on these lines will be undertaken when circumstances permit. Meanwhile, we have prepared a suitable salt of another type by combining 2-phenyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinoline with *p*-chlorophenacyl bromide to give the highly crystalline 2-*phenyl*-2-p-*chlorophenacyl*-1 : 2 : 3 : 4-*tetrahydroisoarsinolinium bromide* (II), a salt containing an asymmetric arsenic atom. Now the 1 : 2 : 3 : 4-tetrahydro*iso*arsinoline system is known to possess considerable stability (see previous paper); furthermore, many *p*-chlorophenacyl compounds also have marked stability, far greater than that of the corresponding unsubstituted phenacyl compounds * (cf. Crowther and Mann, this vol., p. 58). Hence it was expected that the quaternary arsonium bromide (II) would possess very considerable stability and undergo no dissociation (other than ionisation) in solution, and thus be capable of resolution into optically stable forms.

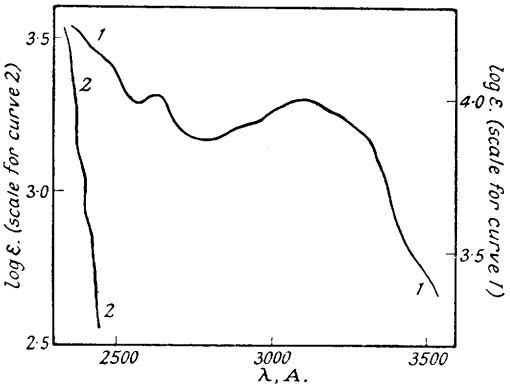
Experiment has fully confirmed our reasoning. The bromide (II) was converted into the d-*bromocamphorsulphonate*, which after recrystallisation from ethyl acetate had m. p. 119—131°, $[M]_D$ + 279° (in chloroform). When, however, this product was extracted with boiling benzene–*cyclo*hexane, the *d-iso*arsinolinium *d*-bromo-

* This difference in stability is well exemplified in the bromides. The pure colourless crystals of phenacyl bromide slowly decompose to a reddish-brown syrup at room temperature even in a dry atmosphere, whereas *p*-chlorophenacyl bromide remains unchanged indefinitely as colourless needles of sharp m. p. under these conditions.

camphorsulphonate dissolved, leaving an insoluble residue of the *l-iso*arsinolinium *d*-bromo-sulphonate, which was readily obtained optically pure by repeated crystallisation from alcohol, and then had m. p. 236—238°, $[M]_D$ — 140°. This salt was converted into l-iso*arsinolinium picrate*, which had $[M]_D$ — 450° (in chloroform), no change in rotation being detected during 24 hours. An acetone solution of this picrate, when treated at 0° with a similar solution of potassium iodide in excess, furnished the crystalline l-iso*arsinolinium iodide*; slight racemisation accompanied this conversion, however, because the iodide so obtained had initially $[M]_D$ — 326°, but recrystallisation from alcohol gave the optically pure iodide having m. p. 176°, $[M]_D$ — 354°, neither constant being changed by further recrystallisation. (For rotations at other wave-lengths, see p. 554.) It is noteworthy that the *dl*-iodide had m. p. 190·5°.

The crude *d-iso*arsinolinium *d*-bromocamphorsulphonate, which had dissolved in the hot benzene–*cyclo*hexane, when isolated had $[M]_D$ + 575° in chloroform and gave the *d-iso*arsinolinium picrate, $[M]_D$ + 354°. Neither of these compounds was optically pure, but their isolation confirms the separation of the two forms from the original *dl-iso*arsinolinium *d*-sulphonate. The optically pure *d-iso*arsinolinium salts were obtained by converting the original racemic bromide (II) into the *l*-bromocamphorsulphonate. Extraction with benzene–*cyclo*hexane now left the insoluble d-iso*arsinolinium* l-*bromocamphorsulphonate*, which after recrystallisation from alcohol had m. p. 236—237°, $[M]_D$ + 140°; this in turn, furnished the optically pure stable d-iso*arsinolinium picrate*, $[M]_D$ + 457°.

It is noteworthy that the *l-iso*arsinolinium iodide underwent no perceptible racemisation in chloroform solution at 15° during 5 days if protected from bright light, which caused slight photochemical decomposition, nor did any appreciable racemisation occur in boiling alcohol, since this solvent was used for the final purification. On the other hand, partial racemisation always occurred when the picrate was converted into the iodide in acetone solution: this slight racemisation apparently occurred during the actual conversion, since no further racemisation could be detected in acetone solution at room temperature. It was, however, increased considerably in boiling aqueous acetone, a sample of the *l*-iodide losing 9% of its activity after 30 minutes' refluxing in this solution. It is probable therefore that in the boiling acetone slight dissociation did occur, with the regeneration of the original tertiary arsine and *p*-chlorophenacyl iodide.



Absorption of: (1) 2-*phenyl*-2-p-*chlorophenacyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinolinium bromide;* (2) *tetraethylarsonium iodide.*

The reduced arsenical ring in the tetrahydro*iso*arsinolinium ion is undoubtedly "buckled," and this buckling, if rigid, would cause molecular dissymmetry irrespective of individual asymmetric atoms: all stereochemical experience, however, indicates that such buckling would be extremely labile and could not cause molecular dissymmetry, and the optical activity must therefore be due to the asymmetric arsenic atom.

Dr. C. B. Allsopp has kindly investigated the optical properties of the *iso*arsinolinium iodide, and we are indebted to him for the following report:

"The optical rotations observed in the visible spectrum for 4 dm. of a 0·520% solution of *l*-2-phenyl-2-*p*-chlorophenacyl-1' : 2 : 3 : 4-tetrahydro*iso*arsinolinium iodide (p. 554) can be represented, within the limits of experimental error, by the simple dispersion equation $\alpha = -0{\cdot}3816/(\lambda^2 - 0{\cdot}0597)$ (see table below). The dispersion constant in this equation suggests that the optical activity originates mainly in electronic transitions which correspond to absorption at about 2443 A., but it would be necessary to carry the observations to shorter wave-lengths before this point could be decided with certainty.

λ, A.	α, obs.	α, calc.	α, obs. — α, calc.	λ, A.	α, obs.	α, calc.	α, obs. — α, calc.
6708	−1·01°	−0·98°	−0·03°	5461	−1·60°	−1·60°	(±)
6104	−1·20	−1·22	+0·02	5086	−1·93	−1·92	−0·01°
5780	−1·40	−1·39	−0·01	4358	−2·93	−2·93	(±)

"The absorption spectrum of racemic 2-phenyl-2-*p*-chlorophenacyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinolinium bromide, as measured with a Hilger 'Spekker' photometer and intermediate quartz spectrograph, is drawn in the figure. It shows an intense band with a maximum, log ε = 4·01, at 3115 A., and more intense absorption at shorter wave-lengths, log ε>4·24 at 2300 A., with a subsidiary maximum, log ε = 4·02, at 2635 A. The spectrum of the iodide is closely similar, but the chromophore absorbing at 3115 A. (presumably the $\cdot CH_2 \cdot CO \cdot C_6H_4Cl$ radical) is photo-sensitive and began to decompose during the measurements, the solution becoming yellow and detail in the spectrum becoming obscured. All the absorption at wave-lengths above 2500 A. may be attributed to the isolated and substituted phenyl residues, but at least part of that at shorter wave-lengths is due to the arsenic atom, since tetraethylarsonium iodide (Curve 2) gives rise to no absorption except at short wave-lengths, when it is about five times weaker. [At 2550 A., the intensity due to this compound is 300 times less (log ε = 1·45) than that due to the aromatic compounds.]

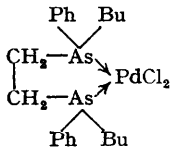
"The calculated anisotropic absorption frequency for the optically active compound lies within this absorp-

tion band, so it is possible that the optical anisotropy of *l*-2-phenyl-2-*p*-chlorophenacyl-1 : 2 : 3 : 4-tetrahydro-*iso*arsinolinium iodide is centred in an electron of the asymmetric arsenic atom. In this it would differ from that of optically active carbon compounds in which the anisotropy is often found to be largely confined to a weakly absorbing chromophoric substituent."

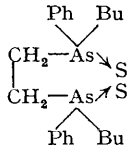
In contrast to the ready resolution afforded by the *iso*arsinolinium bromocamphorsulphonates, it is noteworthy that no evidence of resolution could be obtained in earlier experiments by the recrystallisation of the corresponding *d*-camphorsulphonate.

The optical stability of our *l-iso*arsinolinium iodide in chloroform solution, taken in conjunction with the chemical stability of the *iso*arsinolinium salts, thus affords strong evidence in favour of the dissociation theory of optical instability of quaternary arsonium halides.

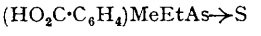
The fundamental factor determining the optical stability of other types of 4-covalent arsenic derivatives is, however, not so clear. Chatt and Mann (J., 1939, 1622) separated ethylene-αβ-bis(phenyl-*n*-butylarsine)-dichloropalladium (III) into two isomeric forms, one of which must have been the *meso* and the other the racemic compound; the two forms possessed great stability, and no interconversion occurred either in the molten condition or on prolonged boiling in alcoholic solution. This marked stability is to be expected in



(III.)



(IV.)



(V.)

this compound, because the co-ordinated ring, for dimensional and structural reasons, is itself very stable, and no dissociation therefore apparently occurs. The corresponding ethylene-αβ-bis(phenyl-*n*-butylarsine sulphide) (IV) was also separated into two similar forms (Chatt and Mann, J., 1939, 610), but in this case the low-melting form very readily passed over into the high-melting form, a conversion which must have entailed a change of configuration of one of the asymmetric arsenic atoms. This result is in marked contrast to those of Mills and Raper (J., 1925, **127**, 2479), who resolved methylethyl-*p*-carboxyphenylarsine sulphide (V) into optically active forms having considerable stability, and no racemisation of these compounds has been recorded. It is possible that in these 4-covalent arsine sulphides, racemisation is similarly dependent on partial dissociation into tertiary arsine and sulphur, and will therefore be dependent in turn on the chemical stability of the particular compound investigated.

If this is true, the ready conversion of the low-melting form of the diarsine disulphide (IV) into the high-melting form is not unexpected. It is well known that if two or more tertiary nitrogen, phosphorus, or arsenic atoms occupy neighbouring positions in a molecule, it is often very difficult to make all these atoms exert simultaneously a covalency of four. This is true, *e.g.*, of the two arsenic atoms in both forms of 5 : 10-di-*p*-tolyl-5 : 10-dihydroarsanthren (Chatt and Mann, J., 1940, 1184) and of the four nitrogen atoms in tetrakis-dimethylaminomethylmethane (Gibson and Mann, J., 1942, 175) : many similar instances could be quoted. The explanation of this comparative inertness is doubtless that when, for example, the first arsenic atom in the arsanthren forms a methiodide, the positive charge on this atom exerts a very strong inductive effect, which in turn reduces considerably the normal reactivity of the lone pair of electrons on the second arsenic atom, which consequently becomes inert. The charge on each arsenic atom in the diarsine disulphide (IV) is, however, much weaker than that on a quaternary arsonium atom, and hence does not prevent both atoms showing simultaneously this form of 4-covalency. Nevertheless, the effect must be present, and will facilitate the dissociation, diarsine disulphide $\rightleftarrows$ diarsine monosulphide + sulphur. Even if this equilibrium dissociation should occur only to a minute extent, it will explain the conversion of the less stable form of the disulphide into the more stable.

Experimental.

All rotations were measured in a 4-dm. tube at 16° with (unless otherwise stated) chloroform as solvent, and the sodium-*D* line, λ 5893, as the source of light.

dl-2-*Phenyl*-2-p-*chlorophenacyl*-1 : 2 : 3 : 4-*tetrahydroisoarsinolinium Bromide* (II).—A benzene solution of 2-phenyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinoline (1 mol.) and *p*-chlorophenacyl bromide (1 mol.) was refluxed for 30 mins., separation of the crystalline salt gradually occurring. The mixture was cooled, and the *bromide* (II) collected, washed with benzene, and recrystallised from alcohol; m. p. 190—191° (Found : C, 54·2; H, 4·2. $C_{23}H_{21}OClBrAs$ requires C, 54·8; H, 4·2%). Yield, 80—90% of the theoretical.

The corresponding dl-*iodide* was prepared by the following indirect method. A cold chloroform solution of the bromide was repeatedly shaken with a saturated aqueous solution of sodium picrate. During the fourth extraction, the *iso*arsinolinium picrate separated as a yellow solid, and was collected and washed with water. Evaporation of the chloroform gave a further quantity. An acetone solution of this picrate was then treated with excess of potassium iodide dissolved in acetone containing a few drops of water. The iodide (as II) slowly crystallised, and was then collected, washed with acetone until colourless, and recrystallised from alcohol; m. p. 190·5° (Found : C, 50·2; H, 3·6. $C_{23}H_{21}OClIAs$ requires C, 50·1; H, 3·8%).

The d-*bromocamphorsulphonate* was prepared by gently boiling a solution of the bromide (1 mol.) and silver *d*-bromocamphorsulphonate (1 mol.) in 80% alcohol for 10 minutes, and then evaporating the filtered solution to dryness. The glassy residue was very soluble in methyl and ethyl alcohol, acetone, chloroform, and ethyl acetate; a portion, when dissolved in ethyl acetate and set aside, slowly deposited the crystalline salt. The remainder of the glass was boiled with *cyclo*hexane, and benzene cautiously added until a clear solution was obtained; this solution, when slowly cooled

and seeded with the above crystals, deposited the *d*-bromocamphorsulphonate as white crystals, m. p. 119—131° after softening at 115° (Found : C, 54·4; H, 5·0. $C_{33}H_{35}O_5ClBrSAs$ requires C, 54·0; H, 4·8%). A 1·015% solution had $\alpha + 1{\cdot}54°$, $[M] + 279°$.

Further recrystallisation from benzene–*cyclo*hexane was attempted, but complete solution could not be obtained. The insoluble residue, after thorough extraction with the boiling mixed solvent, was collected and recrystallised from alcohol, the optically pure l-iso*arsinolinium* d-*bromocamphorsulphonate* being readily obtained. The final product of the following crystallisations had m. p. 236—238° with slight previous softening (Found : C, 53·9; H, 4·8%) :

	Concn. of solution, %	α.	[α].	[M].
Once recrystallised	1·198	−0·81°	−17°	−120°
Three times recrystallised	1·270	−0·95	−19	−140
Four times recrystallised	1·160	−0·87	−19	−140

A cold chloroform solution of this pure *l-iso*arsinolinium *d*-sulphonate was shaken with a saturated aqueous solution of sodium picrate for 30 mins.; the chloroform layer, which had become yellow, was separated, and the treatment repeated six times. The chloroform solution of the l-iso*arsinolinium picrate* was then twice washed with water, dried, and evaporated at room temperature; the picrate remained as a friable glass (Found : N, 6·3. $C_{29}H_{23}O_8N_3ClAs$ requires N, 6·45%). A 0·551% solution in chloroform had $\alpha - 1{\cdot}52°$ $[M] - 450°$, and a 0·549% solution in acetone $\alpha - 1{\cdot}135°$, $[M] - 337°$; these rotations were unchanged after the solutions had remained at room temperature for 24 hours.

The l-iso*arsinolinium iodide*. Solutions of the above picrate (2·3 g.) in acetone (80 c.c.) and of potassium iodide (1 g.) in acetone (60 c.c.) containing water (2 c.c.) were mixed at 0° and stirred during 15 mins. The *iodide* (1·7 g.) which had slowly crystallised was then collected and washed with acetone until colourless; m. p. 178·5—179° with darkening from 170° (Found : C, 50·4; H, 4·0; Cl, 6·4; I, 22·8. $C_{23}H_{21}OClIAs$ requires C, 50·1; H, 3·8; Cl, 6·45; I, 23·1%. The Cl and I were calculated from a total halogen estimation, on the assumption that they were present in equiatomic proportion). A 0·519% solution had $\alpha - 1{\cdot}23°$, $[M] - 326°$.

Another preparation of the iodide was carried out precisely as above, for confirmation (Found : C, 49·9; H, 4·1%). A 0·547% solution had $\alpha - 1{\cdot}37°$, $[M] - 345°$. The rotation was unchanged after this solution had been kept in the dark at room temperature for 5 days. On exposure to daylight, however, slight decomposition occurred and the solution became yellow; after 15 hours' exposure, the rotation had fallen to $\alpha - 1{\cdot}22°$, $[M] - 307°$.

The iodide was then crystallised from alcohol until it was optically pure; after one recrystallisation, a 0·517% solution had $\alpha - 1{\cdot}33°$, $[M] - 345°$, and after two recrystallisations, a 0·508% solution had $\alpha - 1{\cdot}30°$, $[M] - 352°$. This pure *l*-iodide had m. p. 176° (Found : C, 50·5; H, 3·8; ionic I, 23·3%. The ionic iodine was estimated volumetrically as described for the phenylmethyl analogue; see previous paper, p. 549).

A 0·520% solution of this iodide gave the following rotations .

Source of light.	A.	α.	[M].	Source of light.	A.	α.	[M].	Source of light.	A.	α.	[M].
Li	6708	−1·01°	−267°	Hg	5780	−1·40°	−370°	Cd	5086	−1·93°	−511°
Li	6104	−1·20	−318	Hg	5461	−1·60	−423	Hg	4358	−2·93	−776

A solution of this pure *l*-iodide (0·5 g.) in a mixture of acetone (32·5 c.c.) and water (1·5 c.c.) was refluxed for 10 mins., the colourless crystals at first forming a white opaque mat but later giving a clear solution. The latter on cooling deposited the iodide (0·45 g.) chemically unchanged, but partly racemised (Found : C, 50·3; H, 4·1%). A 0·416% solution had $\alpha - 0{\cdot}97°$, $[M] - 320°$.

To obtain the *d-iso*arsinolinium ion, the benzene–*cyclo*hexane which had been used to extract the original bromocamphorsulphonate was evaporated to dryness, and the glassy residue extracted with a very small volume of cold alcohol. A small residue was filtered off, and the solution evaporated again to dryness; the glassy product consisted of the optically impure *d-iso*arsinolinium *d*-bromocamphorsulphonate : a 1·095% solution had $\alpha + 3{\cdot}43°$, $[M] + 575°$. This was converted, as already described, into the optically impure *d*-picrate, a 0·553% solution of which had $\alpha + 1{\cdot}20°$, $[M] + 354°$.

The optically pure *d-iso*arsinolinium compounds were obtained by repeating the original resolution, using silver *l*-bromocamphorsulphonate. Extraction of the *iso*arsinolinium *l*-sulphonate with benzene–*cyclo*hexane, followed by repeated alcoholic recrystallisation of the insoluble residue, gave the pure d-iso*arsinolinium* l-*bromocamphorsulphonate*, colourless needles, m. p. 236—237° (Found : C, 54·1; H, 4·8%); a 1·193% solution had $\alpha + 0{\cdot}89°$, $[M] + 140°$. This compound, treated as before, gave the pure d-iso*arsinolinium picrate* (Found : N, 6·1%); a 0·570% solution had $\alpha + 1{\cdot}60°$, $[M] + 457°$.

2-*Phenyl*-2-p-*chlorophenacyl*-1 : 2 : 3 : 4-*tetrahydro*iso*arsinolinium* d-*Camphorsulphonate*.—This was prepared in hot aqueous-alcoholic solution precisely as for the bromocamphorsulphonate. The clear filtrate, when evaporated to dryness, gave at once the crystalline d-*camphorsulphonate*; this was very soluble in methyl and ethyl alcohol, but almost insoluble in ethyl acetate and acetone. It was therefore recrystallised from ethyl alcohol containing 66% of water, from which it tended to separate as an oil which rapidly crystallised on scratching; m. p. 210—212° (Found : C, 59·7; H, 5·5. $C_{33}H_{36}O_5ClSAs$ requires C, 60·5; H, 5·5%). It was repeatedly recrystallised from the aqueous alcohol, without change in m. p.; the fractions obtained (*a*) from the 6th, (*b*) from the 7th recrystallisation, and (*c*) from evaporation of the mother-liquors from the 3rd recrystallisation, gave the following rotations, in 2·347, 2·427, and 1·802% solutions respectively : $\alpha + 1{\cdot}58°$, $1{\cdot}65°$, $1{\cdot}23°$, $[M] + 110°$, $111°$, $112°$.

To determine if resolution was proceeding, an alcoholic solution of the final fraction was treated with the calculated quantity of chloroplatinic acid. The very pale orange iso*arsinolinium chloroplatinate* was collected, and washed with alcohol, water, and alcohol in turn : m. p. 135—150° (decomp.) (Found : C, 43·4; H, 3·1. $C_{46}H_{42}O_2Cl_8As_2Pt$ requires C, 44·0; H, 3·35%). A 2·327% chloroform solution had $\alpha + 0{\cdot}05°$, $[M] + 7°$. No significance is attached to these minute rotations.

This chloroform solution, when set aside overnight, deposited orange needles, and lost its minute rotation. The needles were insoluble in all the usual solvents, and had m. p. 211—213° with softening at 105° (Found : C, 36·3; H, 3·2%). This curious change was not further investigated.

The final fraction of the *d*-camphorsulphonate was similarly converted into the yellow crystalline *chloroaurate*, m. p. 157—158° (Found : C, 35·9; H, 2·8; Au, 26·55. $C_{23}H_{21}OCl_5AsAu$ requires C, 36·2; H, 2·75; Au, 25·8%). A 2·02% solution in acetone showed no activity.

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