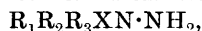


CLXXXIII.—*Studies in Substituted Quaternary Azonium Compounds Containing an Asymmetric Nitrogen Atom. Part II. Resolution of Phenylbenzylmethylazonium Iodide into Optically Active Components.*

By BAWA KARTAR SINGH.

IN the present paper the resolution of another enantiomorphous compound the optical activity of which is due to the presence of an asymmetric nitrogen atom is described. The author has already shown (T., 1913, **103**, 604) that phenylmethylethylazonium iodide is capable of resolution, but as the value of the molecular rotatory power of the phenylmethylethylazonium ion is low, it was thought that it would be desirable to extend this new series,



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by the resolution of other members possessing high rotation constants, thereby also accumulating data connecting constitution with optical rotatory power. With this object the resolution of phenylbenzylmethylazonium iodide was undertaken.

The azonium iodide referred to above was produced in two different ways, namely, by the action of methyl iodide on phenylbenzylhydrazine and of benzyl iodide on phenylmethylhydrazine. The asymmetric azonium iodide was the main product of both the reactions, besides small amounts of by-products which were formed owing to substitution having taken place.

It may be suggested that phenylbenzylmethylazonium iodide may dissociate into the three secondary hydrazines, the formation of which is possible, namely, phenylmethylhydrazine, benzylmethylhydrazine, and phenylbenzylhydrazine, and the corresponding alkyl iodides, and these combinations, in turn, are capable of giving rise to different substituted azonium iodides having two similar radicles, but that in the action of benzyl iodide on phenylmethylhydrazine, under the experimental conditions, benzyldimethylazonium iodide is the only by-product.

Other instances of displacement of alkyl groups similar to the above have been recorded in the cases of the quaternary ammonium compounds (Pope and Read, T., 1912, **101**, 519; Jones, T., 1903, **83**, 1408; 1905, **87**, 1721; and Wedekind, *Ber.*, 1905, **38**, 438), as well as in those of sulphonium compounds (Dehn, *Annalen Suppl.*, **4**, 83).

The thermal decomposition of phenylbenzylmethylazonium hydroxide has also been studied. It is found that in aqueous alcoholic solution the azonium hydroxide decomposes on heating at the temperature of the water-bath into phenylbenzylhydrazine and methyl alcohol. The secondary hydrazine was identified as its hydroferrocyanide, and in this connexion it may be mentioned that a general method for the identification of secondary hydrazines by means of their hydroferrocyanides is developed. These compounds have not hitherto been investigated, and in order to establish their composition they were directly prepared for this purpose.

Resolution.—The resolution of phenylbenzylmethylazonium iodide was effected by means of Reychler's silver *d*-camphor- β -sulphonate, and Armstrong and Lowry's silver *d*- α -bromocamphor- β -sulphonate (T., 1902, **81**, 1441). The hydrogen *d*-tartrate could only be obtained as an oil, which could not be crystallised.

Pope and Read recognised (T., 1910, **97**, 987) that three cases may occur when an externally compensated base is crystallised with an optically active acid: (1) the two salts, *d*B*d*A and *l*B*d*A, crystal-

lise separately, so that each may be readily isolated; (2) a partly racemic compound, $dB/B, 2dA$, may be formed, in which case resolution is impossible; (3) each crystal which separates may contain both salts, $dAdB$ and dA/B , but in varying proportions; in other words, the two salts form solid solutions one in the other, which can only be partly separated by prolonged fractional crystallisation. Type 3 is well illustrated in the crystallisation of externally compensated sodium 1-methylcyclohexylidene-4-acetate with brucine hydrochloride (Perkin, Pope, and Wallach, T., 1909, **95**, 1790; Pope and Read, T., 1910, **97**, 987), and similar behaviour is met with in the cases of the camphor- β -sulphonate and α -bromocamphor- β -sulphonate of phenylbenzylmethylazonium. In the case of the camphorsulphonate, when about one-sixth of the salt $dAdB$ (melting point 177°) has separated out in an almost pure condition (see experiment 1, p. 1980), the next fractions exhibit molecular rotatory powers, $+36.4^\circ$ and $+28.57^\circ$; these, therefore, consist of 43.9 and 40.6 per cent. respectively of $dAdB$ salt, the rest being made up of the $lBdA$ component. In the second experiment with the same salt (see p. 1980) about one-eighth of the salt $dBdA$ separates out in an almost pure condition. The last fractions exhibit molecular rotatory powers, $+34.5^\circ$ and $+30.9^\circ$, and, therefore, consist of the two salts $dAdB$, dA/B , in the form of their solid solutions one in the other, containing 43 and 41.5 per cent. of the $dBdA$ component respectively. The points bearing on the lowering of the melting point obtained in experiments 1 and 2 may be considered as follows:

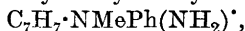
As the amount of the salt $lBdA$ increases in the solid solution, the melting point falls to $172-173^\circ$ and $168-169^\circ$, having values for $[M]_D +36.4^\circ$ and $+34.5^\circ$, thus containing 43.9 and 43 per cent. of the salt $dBdA$. The melting point again rises to 171° with $[M]_D +28.57^\circ$, and thus containing 40.6 per cent. of the salt $dBdA$. This, therefore, suggests that the eutectic mixture of the two salts above referred to melts in the neighbourhood of $167-168^\circ$, and thus consists of about 41.5 per cent. of the salt $dBdA$ and 58.5 per cent. of $dAdB$.

In the case of the bromocamphorsulphonate about one-third of the salt $dBdA$ separates out in an almost pure condition. The next fractions which are obtained have molecular rotatory powers ranging from $+247^\circ$ to $+261^\circ$. Further crystallisations in different solvents and at lower temperature do not bring about any appreciable resolution. From this it must be concluded that the two component salts have here also formed solid solutions one in the other. The pure $dBdA$ salt melts at 197° , and as the amount of $lBdA$ component increases in the solid solution, the melt-

ing point falls to $175\text{--}178^\circ$ with $[M]_D + 325.1^\circ$, and thus consisting of about 53.6 per cent. of the salt $dBdA$ and 46.4 per cent. of the salt $lBdA$. The original unresolved salt consisting of 50 per cent. of each component melts at $173\text{--}175^\circ$. The melting point further falls to $165\text{--}166^\circ$ with $[M]_D + 261.5^\circ$, thus consisting of about 21.5 per cent. of the salt $dBdA$ and 78.5 per cent. of the salt $lBdA$. It again rises to $167\text{--}168^\circ$ with $[M]_D + 253.5^\circ$, thus corresponding with about 17.4 per cent. of the salt $dBdA$ and 82.6 per cent. of $lBdA$. It follows, from the above, that the eutectic mixture melts in the neighbourhood of $165\text{--}166^\circ$.

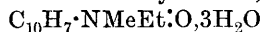
It has been pointed out above that the first fractions of highest melting point represent the $dBdA$ components in the pure state. This statement is further supported by the fact that the d -picrates obtained from the camphorsulphonate and the bromocamphor sulphonate give identical values for the molecular rotatory power, thus indicating that complete resolution has taken place in the case of the first fractions. In this connexion it may be pointed out that in view of the difficulties which are experienced in resolving externally compensated compounds, the importance of working with more than one optically active salt for resolution cannot be over-estimated. This need becomes still more apparent when it is remembered that there is no quantitative relation connecting optical rotation constants with constitution.

The d - β -camphorsulphonate gives the maximum molecular rotatory power for the d -phenylbenzylmethylazonium ion,



as $[M]_D$ about $+119^\circ$ in aqueous solution; the d - α -bromocamphor- β -sulphonate as about $+99^\circ$, the d -iodide as about $+98^\circ$, both in methyl alcohol; and the d -picrate as about $+89^\circ$ in methyl alcohol, and about $+254^\circ$ in chloroform solution. These values present a very marked contrast to the maximum rotation constant for the l -phenylmethylethylazonium ion as $[M]_D$ about -30° (*loc. cit.*). It may, therefore, be inferred that the ethyl group has a great inhibiting effect on the value of the rotation constant, and this conclusion becomes strengthened when a similar comparison is made in the case of the quaternary asymmetric ammonium compounds. The ethyl compound of the phenylbenzylmethylammonium series has for the asymmetric ammonium ion $[M]_D$ about $+64^\circ$, the propyl and the isopropyl compounds have -299° and -398° respectively. In the phenylmethylallylammonium series the ethyl compound gives for the basic ion, $[M]_D + 16^\circ$, and the n -propyl and the isopropyl compounds give $[M]_D + 106^\circ$ and -103° respectively. Yet in another class of compounds, namely, those investigated by Meisenheimer, the value of $[M]_D$ for hydroxyphenylmethylethylammonium

chloride, $\text{OH}\cdot\text{NMeEtPhCl}$ (*Ber.*, 1908, **41**, 3966), and for hydroxy- β -naphthylmethylethylammonium hydroxide,



(*Annalen*, 1911, **385**, 117) is only 41° and 39° respectively. The above comparison clearly points to a constitutive effect, which is conditioned to some extent at least by the presence of an ethyl group in the molecule.

No mutarotation has been observed in the case of the compounds described in the present paper, either on keeping or on heating their solutions. This is the more remarkable as solutions of the salts of phenylmethylethylazonium undergo inversion on keeping (*loc. cit.*). The influence of solvents on the rotation constants of phenylbenzylmethylazonium salts is very marked. The molecular rotatory power is almost three times as great in chloroform as in methyl alcohol or acetone.

The *dl*-salts have, in all the cases examined, higher melting points than the corresponding *d*-salts. It may, therefore, be concluded that they are not *dl*-mixtures (conglomerates), although the question as to whether they are racemic compounds or pseudo-racemic mixed crystals is left open.

EXPERIMENTAL.

Phenylbenzylmethylazonium Iodide, $\text{C}_7\text{H}_7\cdot\text{NMePhI}\cdot\text{NH}_2$.

This substance was prepared by two different methods:

(a) *By the Action of Methyl Iodide on Phenylbenzylhydrazine.*—Phenylbenzylhydrazine (20 grams) was mixed with one molecular proportion of methyl iodide (15 grams) in the presence of a little ether; the mixture was cooled in ice, and the white, crystalline substance which separated overnight (10.2 grams), on recrystallisation from hot alcohol, melted and decomposed at 122° .

The mother liquor, on keeping for ten days, deposited a very small quantity of a crystalline material (about 0.2 gram), which after recrystallisation from alcohol and ether melted and decomposed at $186\text{--}187^\circ$:

0.2077 gave 0.1857 AgI. $I=48.31$.

The substance cannot be phenyldimethylazonium iodide (which requires $I=48.1$ per cent.), for the latter melts and decomposes at $126\text{--}127^\circ$, as is shown below.

(b) *By the Action of Benzyl Iodide on Phenylmethylhydrazine.*—An ice-cold ethereal solution of phenylmethylhydrazine (25 grams) was added to one molecular proportion of an ethereal solution of benzyl iodide (45 grams), also cooled in ice. The crude product (34.5 grams), after recrystallisation from hot alcohol, melted and decomposed at 122° . The azonium iodide turns red a few degrees

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below its melting point. A mixture of the azonium iodide obtained by the two different methods gave the same melting point; the second method of preparation gave much the better yield. It is soluble in methyl alcohol or acetone, less so in ethyl alcohol or chloroform, very sparingly so in cold water, and insoluble in benzene or ether:

0.3837 gave 0.2650 AgI. $I=37.32$.

0.2189 „ 0.3990 CO_2 , 0.1077 H_2O , and 0.0816 I (by Dumas's method). $C=49.7$; $H=5.44$; $I=37.28$.

$\text{C}_{14}\text{H}_{17}\text{N}_2\text{I}$ requires $C=49.4$; $H=5.0$; $I=37.35$ per cent.

It may be pointed out that the cooling and dilution of the reaction mixture with ether are both essential for the formation of the quaternary azonium iodide. If they are omitted, the reaction becomes very violent owing to rise of temperature with copious evolution of irritating vapours of benzyl iodide. Only a dark, tarry product remains behind, from which no crystalline substance can be isolated.

The mother liquor from the action of benzyl iodide on phenylmethylhydrazine yielded a small, crystalline crop (2.3 grams) of higher melting point. It was recrystallised three times from hot alcohol, and melted and decomposed at 125° . This salt does not turn red below its melting point, but only acquires a yellow colour:

0.1359 gave 0.1947 CO_2 and 0.0680 H_2O . $C=39.07$; $H=5.56$.

0.1165 „ 9.9 c.c. N_2 (moist) at 27° and 761.6 mm. $N=9.45$.

0.1750 „ 0.1479 AgI. $I=45.67$.

$\text{C}_9\text{H}_{15}\text{N}_2\text{I}$ requires $C=38.84$; $H=5.4$; $N=10.07$; $I=45.61$ per cent.

The above analytical data agree with those for *benzyltrimethylazonium iodide*.

dl-Phenylbenzylmethylazonium chloride crystallises in thin, colourless prisms, which melt and decompose at $158-159^\circ$. It is very readily soluble in water or alcohol, but insoluble in benzene or ether:

0.39655 gave 0.23015 AgCl. $\text{Cl}=14.36$.

$\text{C}_{14}\text{H}_{17}\text{N}_2\text{Cl}$ requires $\text{Cl}=14.28$ per cent.

The corresponding *platinichloride* crystallises from boiling water acidified with hydrochloric acid in orange-coloured needles melting and decomposing at 162° . It is insoluble in cold water, as well as in organic solvents, but dissolves in much boiling water:

0.2182 gave 0.0507 Pt. $\text{Pt}=23.23$.

$(\text{C}_{14}\text{H}_{17}\text{N}_2)_2\text{PtCl}_6$ requires $\text{Pt}=23.40$ per cent.

The *aurichloride* is almost insoluble in cold water, but dissolves in boiling water, from which solvent, in the presence of hydrochloric

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acid, it separates in yellow, stout prisms, melting and decomposing at 134° :

0.2151 gave 0.07715 Au. Au=35.87.

$C_{14}H_{17}N_2AuCl_4$ requires Au=35.71 per cent.

The *hydroferrocyanide*, $(C_7H_7 \cdot NMePh \cdot NH_2)_3, H_5Fe(CN)_{12}$, is almost insoluble in water or organic solvents, and is obtained as a white precipitate by mixing aqueous solutions of potassium ferrocyanide and the azonium chloride in the presence of a mineral acid. It does not melt, but decomposes gradually on heating. In composition it corresponds with an acid salt:

0.3404 gave 0.0531 Fe_2O_3 . Fe=10.9.

$C_{54}H_{56}N_{18}Fe$ requires Fe=10.46 per cent.

The *hydroferricyanide*, $(C_7H_7 \cdot NMePh \cdot NH_2)_2, HFe(CN)_6$, is soluble in water or methyl alcohol, insoluble in chloroform or ether, and crystallises in yellow prisms, which melt and decompose at 140° . In composition it also corresponds with an acid salt:

0.3006 gave 0.0379 Fe_2O_3 . Fe=8.81.

0.0684 „ 12.9 c.c. N_2 (moist) at 23.5° and 763 mm. N=21.29.

$C_{34}H_{35}N_{10}Fe$ requires Fe=8.74; N=21.92 per cent.

$C_{34}H_{35}N_{10}Fe, H_2O$ requires Fe=8.5; N=21.31 per cent.

As the salt, on keeping in the steam-oven, undergoes decomposition with change of colour, its water of crystallisation could not be directly determined.

dl-Phenylbenzylmethylazonium Mercuri-iodides.

I. $(C_7H_7 \cdot NMePhI \cdot NH_2)_2, HgI_2$, prepared from the azonium iodide and mercuric iodide (one-half molecular proportion), crystallises from methyl alcohol in colourless prisms, melting and decomposing at $135-136^{\circ}$ to a green liquid. It is very readily soluble in acetone, moderately so in methyl alcohol, sparingly so in cold alcohol, but more so in hot, and is insoluble in ether or water:

0.2765 gave 11.65 c.c. N_2 (moist) at 22° and 765.6 mm. N=4.81.

$C_{28}H_{34}N_4I_4Hg$ requires N=4.94 per cent.

II. $C_7H_7 \cdot NMePhI \cdot NH_2, HgI_2$, prepared from one molecular proportion of mercuric iodide, separates from alcohol in yellow prisms, melting and decomposing at $128-129^{\circ}$ to a green liquid. It is very readily soluble in acetone or methyl alcohol, sparingly so in ethyl alcohol, and insoluble in ether, chloroform, or water:

0.1725 gave 5.6 c.c. N_2 (moist) at 24° and 762.8 mm. N=3.66.

$C_{14}H_{17}N_2I_3Hg$ requires N=3.53 per cent.

The *dl-picrate*, $C_7H_7 \cdot NMePh(NH_2) \cdot O \cdot C_6H_2O_6N_3$, crystallises from alcohol in yellow prisms, melting and decomposing at 152° . It is very readily soluble in acetone, moderately so in methyl alcohol,

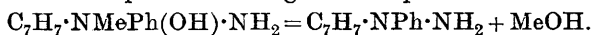
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somewhat less so in cold alcohol or chloroform, but more so in hot; it is insoluble in ether or water:

0.0920 gave 12.8 c.c. N_2 (moist) at 23.5° and 763.5 mm. $N=15.72$.

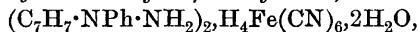
$C_{20}H_{19}O_7N_5$ requires $N=15.87$ per cent.

The *azonium hydroxide*, $C_7H_7 \cdot NMePh(OH) \cdot NH_2$, is strongly alkaline, and can only be obtained as a syrup. Its alcoholic solution, on being heated on the water-bath for some time, becomes turbid, and decomposes according to the equation:



Contrary to expectation, the methyl group is eliminated, and the heavier benzyl radicle remains attached to the nitrogen atom. The secondary hydrazine was identified as its hydroferrocyanide (Found, $Fe=8.63$; $N=21.50$. Calc., $Fe=8.61$; $N=21.61$ per cent.).

Phenylbenzylhydrazine hydroferrocyanide,



separates as an amorphous, white precipitate by mixing an aqueous solution of potassium ferrocyanide with an acidified solution of phenylbenzylhydrazine. It is insoluble in water, but dissolves in alcohol. It does not melt, but begins to decompose gradually on heating:

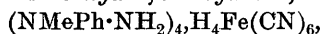
0.2830 gave 0.0347 Fe_2O_3 . $Fe=8.57$.

0.0831 „ 15.5 c.c. N_2 (moist) at 21° and 766 mm. $N=21.41$.

$C_{32}H_{32}N_{10}Fe, 2H_2O$ requires $Fe=8.61$; $N=21.61$ per cent.

As the salt undergoes decomposition in the steam-oven, its water of crystallisation could not be determined, but analyses show that it contains $2H_2O$.

Phenylmethylhydrazine hydroferrocyanide,



is similarly obtained in colourless prisms. It is soluble in cold water, but less so in alcohol.

It does not melt, but decomposes on heating:

0.3030 gave 0.0355 Fe_2O_3 . $Fe=8.19$.

0.1686 „ 0.0192 Fe_2O_3 . $Fe=7.96$.

0.0836 „ 19.5 c.c. N_2 (moist) at 19° and 771.5 mm. $N=27.22$.

0.0794 „ 18.8 c.c. N_2 (moist) at 21° and 769.7 mm. $N=27.31$.

$C_{34}H_{44}N_{14}Fe$ requires $Fe=7.93$; $N=27.85$ per cent.

$C_{34}H_{44}N_{14}Fe, 1H_2O$ requires $Fe=7.73$; $N=27.15$ per cent.

Phenylbenzylmethylazonium d-Camphor- β -sulphonate,



Finely powdered phenylbenzylmethylazonium iodide (30.5 grams) was added in small quantities at a time to one molecular proportion of silver *d*-camphor- β -sulphonate dissolved in boiling ethyl acetate

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moistened with a few drops of water, on the water-bath. The contents of the flask were kept shaken, and after the addition of the whole of the azonium iodide, the heating was continued for some time to complete the reaction. The ethyl acetate was distilled off, and the residue consisting of the azonium camphorsulphonate and silver iodide was extracted with methyl alcohol until only silver iodide remained behind. The camphorsulphonate obtained in this way melted at 170—171°. It is very readily soluble in methyl alcohol or chloroform, moderately so in alcohol or water, sparingly so in benzene, but insoluble in ether:

0.1063 gave 0.2537 CO₂ and 0.0707 H₂O. C=65.09; H=7.39.

C₂₄H₃₂O₄N₂S requires C=64.86; H=7.21 per cent.

The above camphorsulphonate was subjected to fractional crystallisation by dissolving it in the least possible quantity of cold methyl alcohol, and precipitating by gradual addition of ether.

Experiment I was conducted with 12 grams of the substance melting at 170—171°:

Fraction.	Yield in grams.	M. p.	Substance taken in grams.	α_D	$[\alpha]_D^*$	$[M]_D$
A	2.1	175—176°	0.4383	+1.61°	+36.55°	+162.3°
B	2.0	172—173	0.2790	0.23	8.2	36.4
C	4.0	171°	0.2629	0.17	6.43	28.57

Fraction A was subjected to further crystallisations in the same way with the following results:

	α_D	$[\alpha]_D$	$[M]_D$
2nd recrystallisation—m. p. 176°; 0.2931 gram of substance	+1.03°	+34.8°	+154.5°
After 68 hours	1.07	36.5	162.06
3rd recrystallisation—m. p. 176°; 0.3759 gram of substance	1.37	36.2	161.3
After 4 hours	1.38	36.56	162.3
4th recrystallisation—m. p. 176—177°; 0.3455 gram of substance	1.26	36.3	161.2
After 96 hours	1.25	36.0	159.9

The rotatory power was determined in water at 29—30°.

Experiment II was similarly made with 19 grams of salt having $[M]_D + 66.9^\circ$:

Fraction.	Yield in grams.	M. p.	Substance taken in grams.	α_D	$[\alpha]_D$	$[M]_D$
I.	3.2	174—175°	0.1861	+0.56°	29.95°	133.0°
II.	2.1	172—174	0.2669	0.35	13.06	57.95
III.	10.0	167—168	0.1572	0.11	6.96	30.9
IV.	1.4	168—169	0.2334	0.18	7.67	34.5

* The given weight of the substance was dissolved in 19.9 c.c. of the solvent and the rotatory power determination was made in a 2-dm. tube about thirty minutes after solution. This applies to all observations recorded in this paper unless the contrary is stated.

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Fraction I was further submitted to fractional crystallisation with the following result:

	α_D	$[\alpha]_D$	$[M]_D$
3rd crystallisation—m. p. 175—176°; 0.2297 gram of substance	+0.84°	+36.4°	+161.6°
After 16 hours	0.81	35.1	155.8
4th crystallisation—m. p. 177°; 0.1037 gram of substance	0.40	38.4	170.5
After 26 hours	0.40	38.4	170.5

The value of $[M]_D$ was not raised by further crystallisation. The fraction melting at 176—177°, and having $[M]_D + 170^\circ$ represents, therefore, the pure *d*-phenylbenzylmethylazonium *d*-camphor- β -sulphonate.

The rotatory power was determined in water at 29—30°.

Fractions III and IV from the second experiment, and B and C from the first experiment, which amounted to about 17 grams, were mixed together, and had $[M]_D$ ranging from +29° to +36°. These fractions, which contained an excess of the salt of the *laevo*-component of the base, were subjected to a prolonged process of fractional crystallisation, but without any success at further resolution:

	α_D	$[\alpha]_D$	$[M]_D$
1st recrystallisation—m. p. 167—169°; 0.3474 gram of substance	+0.285°	+8.16°	+36.25°
After 6 hours	0.29	8.3	36.9
3rd recrystallisation—m. p. 170—171°; 0.2235 gram of substance	0.17	7.57	33.6
Last fraction (mother liquor)—0.1764 gram of substance	0.16	9.02	40.07

The last value refers to the solid obtained from the mother liquor by evaporating it to dryness in a vacuum desiccator. One more recrystallisation from chloroform and ether gave the following value:

	α_D	$[\alpha]_D$	$[M]_D$
0.2132 gram of substance	+0.18°	+8.44°	+37.49°

It was further recrystallised from acetone and ether, with the following result:

	α_D	$[\alpha]_D$	$[M]_D$
0.4713 gram of substance	+0.37°	+7.81°	+34.68°

The rotatory power was determined in water at 29—30°.

The *iodide*, which was precipitated in colourless prisms from an aqueous solution of the last fraction of the camphorsulphonate by means of potassium iodide, melted and decomposed at 123—124°. Its rotatory power was determined with the following result:

0.1222 in 19.9 c.c. of methyl alcohol gave $\alpha_D - 0.04^\circ$, whence $[\alpha]_D - 3.25^\circ$ and $[M]_D - 11.1^\circ$.

dl-Phenylbenzylmethylazonium d- α -Bromocamphor- β -sulphonate,
 $C_7H_7 \cdot NMePh(NH_2) \cdot O_3S \cdot C_{10}H_{14}OBr$.

This salt was prepared from the azonium iodide, and the silver salt of Armstrong and Lowry's *d*- α -bromocamphor- β -sulphonic acid in the same way as the above-described azonium camphorsulphonate. The bromocamphorsulphonate, obtained in this way, melted at 173—175°; the yield was almost theoretical:

0.1524 gave 0.3052 CO₂ and 0.0861 H₂O. C=54.6; H=6.28.

C₂₄H₃₁O₄N₂BrS requires C=55.06; H=5.93 per cent.

d-Phenylbenzylmethylazonium d- α -Bromocamphor- β -sulphonate.

The bromocamphorsulphonate (25 grams), as obtained in the above way, was subjected to fractional crystallisations as follows:

It was dissolved in the least possible quantity of methyl alcohol, and precipitated by the addition of successive quantities of ether.

Fraction.	Yield in grams.	M. p.	Substance taken in grams.	α_D .	$[\alpha]_D$.	$[M]_D$.
Original unresolved salt	—	173—175°	0.1051	+0.643°	+60.89°	+318.84°
I.	8.9	195°	0.1829	1.45	78.9	412.6
II.	6.9	175—178	0.1180	0.737	62.16	325.1
III.	2.7	165—166	0.1054	0.50	47.22	247.0

The rotatory power was determined in methyl alcohol at 25°.

Fraction II yielded 2 grams of almost pure *dAdB* salt (melting at 196°), which was added to fraction I, and also 3 grams of salt melting at 167—168° added to fraction III.

Fraction I (10.9 grams) was further subjected to a similar process of fractional crystallisation, and its rotatory power was determined in methyl alcohol with the following result:

	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
2nd recrystallisation—m. p. 196—197°;				
0.2657 gram of substance	23°	+2.115°	+79.23°	+414.4°
After 19 hours	23	2.13	79.77	417.3
3rd crystallisation—m. p. 196—197°;				
0.1445 gram of substance	23	1.12	77.11	403.11
4th recrystallisation—m. p. 197°; 0.1111				
gram of substance	24	0.873	78.6	411.8
After 46 hours	25	0.86	77.41	404.8
0.1215 gram of substance (19.9 c.c. of				
chloroform)	28	1.057	86.58	452.8
After 20 hours	26	1.075	88.06	460.5

The fraction melting at 197° represents, therefore, the pure *d*-phenylbenzylmethylazonium *d*- α -bromocamphor- β -sulphonate. It is moderately soluble in methyl alcohol or water, but insoluble in ether or benzene:

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0.1800 gave 0.3641 CO₂ and 0.0946 H₂O. C=55.15; H=5.84.

C₂₄H₃₁O₄N₂BrS requires C=55.06; H=5.93 per cent.

1-Phenylbenzylmethylazonium d-α-Bromocamphor-β-sulphonate.

This salt is left behind in the mother liquor: it could not be obtained in a pure state, as is evident from a determination of its rotatory power.

Fraction III (5.7 grams) was subjected to a prolonged process of fractional crystallisations with the following results:

	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
2nd crystallisation—m. p. 167—168°; 0.0678 gram of substance	24°	+ 0.33°	+ 48.45°	+ 253.5°
3rd crystallisation—m. p. 165—166°; 0.0866 gram of substance	26.5	0.435	49.99	261.5
4th crystallisation—m. p. 166—167°; 0.1222 gram of substance	26.5	0.60	48.86	255.5
5th crystallisation—m. p. 165—166°; 0.1179 gram of substance	27	0.585	49.38	258.2

It is evident from the slow resolution that the two salts *dAdB* and *dAlB* have formed solid solutions one in the other; other solvents like chloroform or acetone and the lower temperature of melting ice were employed for fractional crystallisation, but no further resolution took place. The rotation constants indicate that the above fractions consist of about 19 per cent. of salt *dBdA* and 81 per cent. of *lBdA*. The salt is very readily soluble in methyl alcohol, acetone, or chloroform, less so in ethyl alcohol or water, and insoluble in ether:

0.1172 gave 0.2382 CO₂ and 0.0666 H₂O. C=55.42; H=6.31.

C₂₄H₃₁O₄N₂BrS requires C=55.06; H=5.93 per cent.

d-Phenylbenzylmethylazonium Iodide, C₇H₇·NMePhI·NH₂.

The active iodide was precipitated in white prisms on the addition of a concentrated solution of potassium iodide to an aqueous solution of the camphorsulphonate (m. p. 177° and $[M]_D + 170.5^\circ$); it melted and decomposed at 114°.

Determination of the rotatory power at 28° gave the following result in methyl alcohol:

	α_D .	$[\alpha]_D$.	$[M]_D$.
0.2022 gram of substance.			
After 20 minutes	+ 0.587°	+ 28.89°	+ 98.22°
After 9 hours	0.54	26.58	90.37
After 25 hours	0.49	24.12	82.0
After 53½ hours	0.513	25.35	85.83

At the time of the last observation the solution in the tube had acquired a yellow colour, probably owing to decomposition. The chloroform solution of the active iodide acquired a deep yellow

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colour, and had thus practically cut off most of the light. For this reason the value of the rotation constant was untrustworthy except in indicating that it was much higher than that in methyl alcohol.

d-Phenylbenzylmethylazonium Picrate,
 $C_7H_7 \cdot NMePh(NH_2) \cdot O \cdot C_6H_2O_6N_3$.

The active picrate was prepared by adding a methyl-alcoholic solution of the camphorsulphonate or the bromocamphorsulphonate of the *d*-base to a methyl-alcoholic solution of picric acid. On concentrating the solution, yellow prisms separated, which after one or more crystallisations from alcohol and ether melted and decomposed at 146—147°. The externally-compensated picrate melts at a higher temperature, namely, 152°:

0.0445 gave 6.2 c.c. N_2 (moist) at 20° and 762.5 mm. $N=15.99$.

$C_{20}H_{19}O_7N_5$ requires $N=15.87$ per cent.

The rotatory-power determination made with a sample prepared from the camphorsulphonate gave the following value:

0.0555 gram of substance (in methyl alcohol).	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
After half an hour	25°	+0.215°	+20.27°	+89.35°
After 20 hours	25	0.214	20.19	88.95

The solution was heated to boiling for half-an-hour under reflux, but the rotatory power remained unaltered:

0.0415 gram of substance (in chloroform).	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
After half an hour	21.5°	+0.24	+57.55°	+253.8°
After 80 hours	23	0.23	55.14	243.1

The optical rotatory-power determination made with a sample prepared from the bromocamphorsulphonate gave the following value:

0.0818 gram of substance in 19.9 c.c. of methyl alcohol	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
After half an hour	26°	+0.16°	+19.86°	+87.59°
After 24 hours	26	0.157	19.1	84.22

0.0759 gram of substance in 20.25 c.c. of chloroform	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
After half an hour	26.5°	+0.427°	+56.98°	+251.25°
After 13½ hours	24	0.428	57.11	251.8
After 36 hours	25	0.43	57.38	253.1

The above agreement in the value of the rotatory power of the picrate as obtained from the two different salts indicates that the salt *dAdB* is the pure component. The value of the rotation constant is about three times as large in chloroform as in methyl alcohol.

l-Phenylbenzylmethylazonium Picrate.

This substance, obtained from the bromocamphorsulphonate of the *l*-base, in the same way as its enantiomorphously related isomeride, melts and decomposes at 146° , and is very readily soluble in acetone or methyl alcohol, less so in chloroform, and insoluble in ether or water:

0.1015 gave 13.8 c.c. N_2 (moist) at 24° and 763.4 mm. $N=15.32$.

$C_{20}H_{19}O_7N_3$ requires $N=15.87$ per cent.

The rotatory-power determination gave the following result:

0.1252 gram in methyl alcohol.	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
After half an hour	28°	-0.18°	-14.31°	-63.09°
After 25 hours	26	0.18	14.31	63.09
0.0902 gram in chloroform				
After half an hour	25°	-0.39°	-43.03°	-189.7°
After 65 hours	24	0.38	41.93	184.9

The rotation constants indicate that about 14 per cent. of the *d*-picrate is present in combination with the *l*-picrate.

d-Phenylbenzylmethylazonium Mercuri-iodides.

I. $(C_7H_7 \cdot NMePhI \cdot NH_2)_2 \cdot HgI_2$, obtained from the bromocamphor-sulphonate of the *d*-base, resembles the externally compensated salt, and melts and decomposes at $128-129^{\circ}$:

0.1868 gave 8.2 c.c. N_2 (moist) at 23° and 765.7 mm. $N=4.99$.

$C_{28}H_{34}N_4I_4Hg$ requires $N=4.94$ per cent.

The following rotatory-power determination was made in acetone:

0.2364 gram of substance.	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
After half an hour	26°	$+0.38^{\circ}$	$+16.0^{\circ}$	$+181.4^{\circ}$
After 96 hours	28	0.26	10.94	124.1

At the time of the last observation the solution had acquired a deep yellow colour. The lower value is due to the solution having undergone decomposition. The above rotation constant gives 90.7° as the molecular rotatory power for the single phenylbenzylmethyl-azonium ion.

II. $C_7H_7 \cdot NMePhI \cdot NH_2 \cdot HgI_2$ resembles the externally compensated isomeride, but melts and decomposes at 124° to a green liquid:

0.2312 gave 7.55 c.c. N_2 (moist) at 23° and 765 mm. $N=3.7$.

$C_{14}H_{17}N_2I_3Hg$ requires $N=3.53$ per cent.

The following rotatory-power determination was made in acetone:

0.1437 gram of substance.	Tempera- ture.	α_D .	$[\alpha]_D$.	$[M]_D$.
After half an hour	26°	$+0.16^{\circ}$	$+11.08^{\circ}$	$+87.99^{\circ}$
After 74 hours	26	0.16	11.08	87.99

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The *d-platinichloride* resembles the externally-compensated salt, but melts and decomposes at 154° :

0.2268 gave 0.0534 Pt. Pt=23.54.

$(C_{14}H_{17}N_2)_2PtCl_6$ requires Pt=23.40 per cent.

As the substance is insoluble, its rotatory power could not be determined. There is no doubt, however, that the substance is active, as it melts like other optically active salts, described in this paper, at a lower temperature than the externally-compensated *platinichloride*.

The *d-aurichloride* is readily soluble in methyl and ethyl alcohols, sparingly so in chloroform, and insoluble in ether or water; it melts at $128-129^{\circ}$:

0.3269 gave 0.1168 Au. Au=35.73.

$C_{14}H_{17}N_2AuCl_4$ requires Au=35.71 per cent.

The following rotatory-power determination was made in methyl alcohol solution:

0.1237 gram of substance.	Temperature.	α_D .	$[\alpha]_D$.	$[M]_D$.
After half an hour	24.5°	+0.18°	+14.48°	+79.92°
After 29 hours	24.5	0.19	15.28	84.34

Phenyldibenzylazonium Iodide, $NPh(C_7H_7)_2I \cdot NH_2$.

Phenylbenzylhydrazine (16 grams) was treated with one molecular proportion of a cooled solution of benzyl iodide (18 grams) in ether. The crude product (18.7 grams) on being recrystallised from hot alcohol, melted and decomposed at $133-134^{\circ}$. It is soluble in hot alcohol, very sparingly so in water, and insoluble in ether:

0.3034 gave 0.1695 AgI. I=30.19.

$C_{20}H_{21}N_2I$ requires I=30.53 per cent.

The *aurichloride* is insoluble in water, but dissolves in hot methyl alcohol, and crystallises from the latter solvent in long, yellow prisms, melting and decomposing at $147-148^{\circ}$:

0.2406 gave 0.07535 Au. Au=31.32.

$C_{20}H_{21}N_2AuCl_4$ requires Au=31.40 per cent.

The *platinichloride* is insoluble in water or cold alcohol, but crystallises from hot alcohol in very fine, buff-coloured needles, melting and decomposing at 151° :

0.2184 gave 0.0435 Pt. Pt=19.91.

$(C_{20}H_{21}N_2)_2PtCl_6$ requires Pt=19.77 per cent.

Phenyldimethylazonium Iodide, $NMe_2PhI \cdot NH_2$.

Phenylmethylhydrazine (12.2 grams) was mixed with one molecular proportion of methyl iodide (15 grams) in ethereal solution

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in the cold. The crude product (22 grams), after recrystallisation, separates in colourless, stout prisms, melting and decomposing at 126° . It is very readily soluble in methyl alcohol, moderately so in water, sparingly so in alcohol, and insoluble in chloroform, ether, or benzene:

0.18305 gave 0.1624 AgI. $I=47.94$.

0.2099 „ 0.2817 CO_2 , 0.1011 H_2O , and 0.1004 I. $C=36.6$;
 $H=5.35$; $I=47.83$.

$\text{C}_8\text{H}_{13}\text{N}_2\text{I}$ requires $C=36.37$; $H=4.92$; $I=48.11$ per cent.

The *azonium chloride* is readily soluble in alcohol and water, and is very hygroscopic; it melts and decomposes at $187-188^{\circ}$:

0.1822 gave 0.1509 AgCl. $\text{Cl}=20.49$.

$\text{C}_8\text{H}_{13}\text{N}_2\text{Cl}$ requires $\text{Cl}=20.58$ per cent.

The *platinichloride* crystallises from hot water in yellow prisms, melting and decomposing at $158-159^{\circ}$; it is sparingly soluble in cold water, and insoluble in alcohol:

0.2463 gave 0.07035 Pt. $\text{Pt}=28.57$.

$(\text{C}_8\text{H}_{13}\text{N}_2)_2\text{PtCl}_6$ requires $\text{Pt}=28.60$ per cent.

The *aurichloride* is soluble in alcohol, sparingly so in cold water, and crystallises from hot water in minute, yellow prisms, melting and decomposing at $123-124^{\circ}$:

0.25405 gave 0.1051 Au. $\text{Au}=41.37$.

$\text{C}_8\text{H}_{13}\text{N}_2\text{AuCl}_4$ requires $\text{Au}=41.41$ per cent.

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Further work with other members of the azonium series is in progress.

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