CCCXXXVIII.—*The Constitution of Double Sulphonium Mercuric Iodides. The Optically Active Mercuri-tri- and -tetra-iodides and Cadmi-tetra- and -penta-iodides derived from* l-*Phenacylmethylethylsulphonium Iodide.*

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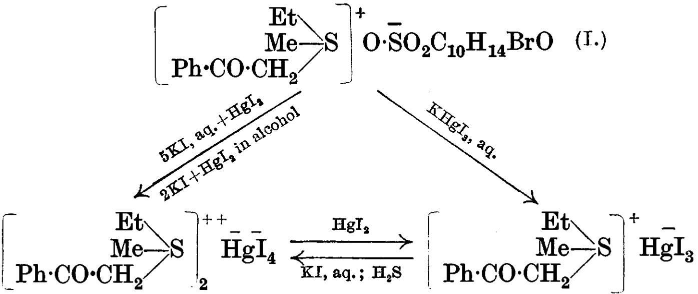
THE double salt formed by the union of potassium iodide (1 mol.) and mercuric iodide (1 mol.) is usually assigned the constitution $K^+[HgI_3]^-$: by analogy, the double sulphonium mercuric iodides have the constitution $R_3S^+[HgI_3]^-$ (Sidgwick, "The Electronic Theory of Valency," p. 227). This constitutional formula is in agreement with the conductivities and the molecular weights of trialkylsulphonium mercuritri-iodides (tri-iodomercuriates) in acetone and also with their parachors (Sudgen, "The Parachor and Valency," p. 154).

Pope and Neville (J., 1902, **81**, 1552), however, proposed an alternative constitutional formula for double sulphonium and selenonium mercuric halides (reproduced in this vol., p. 358) in order to explain why compounds of this type prepared from *d*- and *l*-phenacylmethylethylsulphonium and phenylmethylselenetine *d*-bromocamphorsulphonates were optically inactive.

A study of the chemical properties of the mercuri-tri- and -tetra-iodides and analogous compounds derived from triethylsulphonium and phenyldiethylsulphonium iodides has led to the conclusion that the racemisation of the sulphur compounds of Pope and Neville was due to the chemical instability of sulphonium iodides and to the sensitiveness of sulphonium mercuritri-iodides towards the reagents used in their preparation. As far as it is concerned with *l*-phenacylmethylethylsulphonium mercuritri-iodide, the work of Pope and Neville (*loc. cit.*) has therefore been repeated, with the result that no difficulty has been experienced in obtaining this mercuritri-iodide and other compounds of a similar nature in an optically active condition.

Optically Active Compounds containing Mercuric and Cadmium Iodides in Combination with l-*Phenacylmethylethylsulphonium Iodide.*—Mercuric iodide forms five well-defined salts with cæsium iodide, $CsHgI_3$, Cs_2HgI_4, Cs_3HgI_5, $Cs_2Hg_3I_8$, and $CsHg_2I_5$ (Wells, *Amer. J. Sci.*, 1892, **44**, 221). With *l*-phenacylmethylethylsulphonium iodide, mercuric iodide readily forms double salts which correspond to two members of the cæsium series, *l*-phenacylmethylethylsulphonium mercuritri-iodide (III) and *l*-phenacylmethylethylsulphonium mercuritetraiodide (II).



(I.)

(II.)

(III.)

The methods of preparation and the reactions by which the two compounds can be interconverted are given in the scheme above. The *l*-mercuritri-iodide (III) was obtained by the addition of an aqueous solution (containing a few drops of acetone) of potassium iodide (1 mol.) and mercuric iodide (1 mol.) to an aqueous solution of the *d*-bromocamphorsulphonate (I), prepared by Smiles's method (J., 1900, **77**, 1174). It had m. p. 81—82° and $[\alpha]_{5461}$ − 10·7° in acetone solution. The *l*-mercuritetraiodide (II) was obtained, with m. p. 122—123° and $[\alpha]_{5461}$ − 9·3° in acetone, by the addition of an aqueous-acetone solution of potassium iodide (2 mols.) and mercuric iodide (1 mol.) to the *d*-bromocamphorsulphonate (1 mol.) in ethyl alcohol. To attempt to reconcile the results of the present investigation with the results of Pope and Neville, it was assumed that these authors employed a large excess of potassium iodide. When, however, five molecular proportions of potassium iodide were used to one of mercuric iodide and one of the *d*-bromocamphorsulphonate, with water as the reaction medium, the *l*-mercuritetraiodide was again obtained with $[\alpha]_{5461}$ − 7·9°.

Pope and Neville (*loc. cit.*) record the m. p. of the *dl*-mercuritri-iodide as 128°. The *dl*-mercuri-tri- and -tetra-iodides were therefore prepared for purposes of comparison. The *dl*-mercuritetraiodide was prepared by the addition of an aqueous solution containing potassium iodide (2 mols.) and mercuric iodide (1 mol.) to an alcoholic solution of *dl*-phenacylmethylethylsulphonium bromide (1 mol.). It had m. p. 134° and when allowed to react with mercuric iodide (1 mol.) was converted into the *dl*-mercuritri-iodide, m. p. 82—83°. From these experiments it appears probable that the *dl*-mercuritri-iodide, m. p. 128°, described by Pope and Neville was a slightly impure *dl*-mercuritetraiodide.*

Attempts to prepare the *dl*-phenacylmethylethylsulphonium mercuritrichloride (white scales, m. p. 119°) described by Pope and Neville (*loc. cit.*) have also been unsuccessful, although, as far as can be seen, similar experimental methods have been employed. By the addition of aqueous solutions containing equimolecular quantities of potassium chloride and mercuric chloride (1 and 2 mols.) to aqueous solutions of *dl*-phenacylmethylethylsulphonium *d*-bromocamphorsulphonate (1 mol.), dl-*phenacylmethylethylsulphonium dimercuriheptachloride*, $(Ph\cdot CO\cdot CH_2\cdot SMeEt)_3Hg_2Cl_7$, was obtained in soft white needles, m. p. 153°. The same product was formed in a similar experiment in which an aqueous solution containing potassium chloride (5 mols.) and mercuric chloride (1 mol.) was added to a solution of the *d*-bromocamphorsulphonate of the *dl*-base (1 mol.). From the *d*-bromocamphorsulphonate of the *l*-base (1 mol.), potassium chloride (1 mol.), and mercuric chloride (1 mol.), with water as the reaction medium, l-*phenacylmethylethylsulphonium dimercuriheptachloride* was obtained with $[\alpha]_{5461}$ — 11·3° in methyl-alcoholic solution. This compound has no analogue amongst the cæsium mercuric halides of Wells (*loc. cit.*). It is possible that this salt is composed of equimolecular quantities of the mercuri-tri- and -tetrachlorides, probably chemically linked, since attempts to effect a separation by recrystallisation were fruitless.

From these experimental results, it can be concluded that when an asymmetric sulphonium ion takes part in the formation of a complex double mercuric halide its asymmetry is preserved. It has been found that this is also true when the asymmetric sulphonium ion becomes part of complex double cadmium halides. For example, by the

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* Recently Rây and Adhikary (*J. Indian Chem. Soc.*, 1930, 7, 297) prepared *dl*-phenacylmethylethylsulphonium mercuritri-iodide by Pope and Neville's method and found that its conductivity in acetone solution, in contrast to the conductivity of triethylsulphonium mercuritri-iodide, was of the same order as that of potassium iodide rather than that of potassium mercuritri-iodide. Since these authors record the m. p. of the *dl*-mercuritri-iodide as 129°, it is possible that the compound studied by them was the *dl*-mercuritetraiodide.

addition of aqueous solutions of cadmium iodide (1 mol.) and potassium iodide (either 1 or 2 mols.) to ethyl-alcoholic solutions of the *d*-bromocamphorsulphonate of the *l*-sulphonium base (1 mol.), l-*phenacylmethylethylsulphonium cadmitetraiodide* was obtained with $[\alpha]_{5461}$ − 10·2° in acetone solution. By heating an acetone solution of this *l*-cadmitetraiodide with cadmium iodide, it was converted into l-*phenacylmethylethylsulphonium cadmipentaiodide* with $[\alpha]_{5461}$ − 9·0°.

The Racemisation of the Double Mercuric and Cadmium Halides of the l-*Phenacylmethylethylsulphonium Base.*—Although the empirical compositions of the sulphonium mercuric halides now described differ from those obtained by Pope and Neville, the difference is relatively unimportant. The important difference lies in the fact that, whereas optically active products were consistently obtained in the present research, Pope and Neville isolated products which were optically inactive. The racemisation of the compounds prepared by these authors is probably connected with the instability of sulphonium ions in the presence of halogen ions. This instability is due to the tendency of sulphonium halides to dissociate into an alkyl halide and a sulphide :

$$R_2S + RI \rightleftharpoons [R_3\overset{+}{S}]\overset{-}{I} \xrightarrow{HgI_2} [R_3\overset{+}{S}]Hg\overset{-}{I}_3.$$

Selenonium (Edwards, Gaythwaite, Kenyon, and Phillips, J., 1928, 2293) and telluronium halides (Lowry and Gilbert, J., 1929, 2867) show a similar tendency.

On account of this dissociation, a sulphide, when placed in contact with an equimolecular quantity of an alkyl iodide, is rarely completely converted into a sulphonium iodide : the reaction appears to reach an equilibrium before all the reactants have united. In the presence of mercuric iodide, however, alkyl sulphides and alkyl halides combine more rapidly and completely (Smiles, J., 1900, **77**, 163). The explanation of the action of mercuric iodide is that it converts the iodide ions into stable mercuritri-iodide ions and thereby prevents the disruption of the sulphonium ions. From these considerations it would be expected that *l*-phenacylmethylethylsulphonium mercuritri-iodide would be a stable compound capable of retaining its optical activity in solution. On the other hand, since the mercuritetraiodide ion dissociates into an iodide ion and a mercuritri-iodide ion, it would be expected that the *l*-phenacylmethylethylsulphonium mercuritetraiodide would dissociate in solution according to the following scheme, in which R_3S is the optically active sulphonium ion :

$$[\overset{+}{R}_3\overset{+}{S}]_2H\overset{-}{g}\overset{-}{I}_4 \rightleftharpoons 2[R_3\overset{+}{S}] + H\overset{-}{g}I_3 + \overset{-}{I} : [R_3\overset{+}{S}] + \overset{-}{I} \rightleftharpoons R_2S + RI.$$

This dissociation would lead to the ultimate disruption of all the optically active sulphonium ions and hence solutions of the *l*-mercuritetraiodide should racemise.

These deductions are in agreement with a number of experimental observations. For example, an acetone solution of the *l*-mercuritri-iodide had $[\alpha]_{5461}$ $-$ 10·7° when first prepared and also after it had stood at laboratory temperature for 264 hours. An acetone solution of the *l*-mercuritetraiodide, however, with $[\alpha]_{5461}$ $-$ 7·8° when first prepared, had $[\alpha]_{5461}$ $-$ 2·9° after 41 hours and was optically inactive after 139 hours. Examination of this solution then showed that it contained the *dl*-mercuritetraiodide, as well as methyl ethyl sulphide and other decomposition products of the sulphonium iodide. Similarly, the *l*-cadmi-tetra- and -penta-iodides, both of which contain less stable anions than the mercuritri-iodide anion, gradually lost their optical activity in solution.

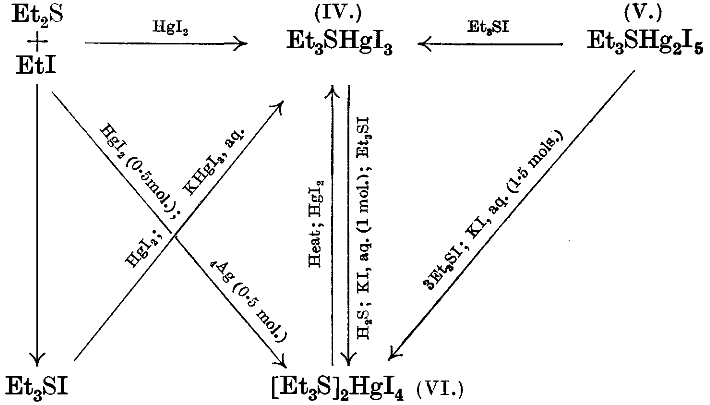
Further, from the scheme given above, it can be concluded that the addition of an alkyl halide to a solution of the *l*-mercuritetraiodide would alter the rate of racemisation, since the alkyl halide, by increasing the concentration of sulphonium iodide, would help to maintain the concentration of iodide ions at a maximum. On the other hand, the addition of an alkyl halide to a solution of the *l*-mercuritri-iodide should be without effect. In agreement with these deductions it was found that a solution of the *l*-mercuritri-iodide containing methyl iodide did not racemise, whereas the addition of methyl iodide to a solution of the *l*-mercuritetraiodide increased its rate of racemisation threefold. A further convincing observation was that a solution containing a mixture of the *l*-mercuri-tri- and -tetra-iodides racemised completely in spite of the fact that the *l*-mercuritri-iodide alone is optically stable.

From this study of the racemisation of these compounds, it can be concluded that, when it is desired to prepare mercuri-iodides of optically active sulphonium bases, the experimental conditions should be so chosen that the mercuri-iodide separates rapidly from the solution and care should be taken that the product is removed as quickly as possible from contact with all solutions containing soluble halides. Pope and Neville were unacquainted with the necessity for these precautions and it is doubtless owing to this cause that their products were optically inactive. As showing the ease with which even the *l*-mercuritri-iodide is racemised by solutions containing iodide ions, the following observation may be recorded. An acetone solution of the *l*-mercuritri-iodide (1 mol.) having $[\alpha]_{5461}$ $-$ 7·8°, had $[\alpha]_{5461}$ $-$ 2·4° immediately after the addition of potassium iodide (5 mols.), and after 15 hours the solution was optically inactive.

During the course of this investigation, solutions of the mercuri-tri-iodide, picrate, and *d*-bromocamphorsulphonate of the *l*-sulphonium base have been kept under observation for periods exceeding 6 months. It has been found that even these compounds suffer a slight but definite loss of rotatory power with lapse of time.

Double Salts derived from Mercuric Iodide and Triethyl- and Phenyl-diethyl-sulphonium Iodide.—The conclusions regarding the relative stabilities of the mercuri-tri- and -tetra-iodide ions are supported by the chemical properties of the mercuri-tri- and -tetra-iodides of the triethyl- and phenyldiethyl-sulphonium bases.

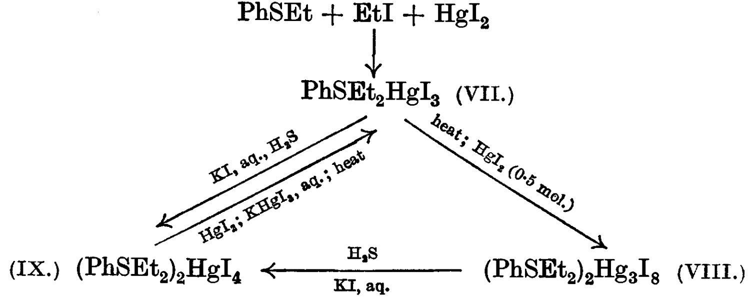
With triethylsulphonium iodide, mercuric iodide readily forms three double salts, Et_3SHgI_3 (IV), $Et_3SHg_2I_5$ (V) (Smiles and Hilditch, J., 1907, **107**, 1394), and $[Et_3S]_2HgI_4$ (VI) (Hofmann and Rabe, *Z. anorg. Chem.*, 1897, **14**, 293). It has been found that these three compounds can be prepared and interconverted by a variety of methods, which are summarised in the following scheme :



It will be seen that (V), the salt containing the highest proportion of mercuric iodide, can be converted into a salt containing a smaller proportion of mercuric iodide by interaction with compounds which will combine with or destroy mercuric iodide, *e.g.*, triethylsulphonium iodide, potassium iodide or hydrogen sulphide. Conversely, (VI), the salt containing the smallest proportion of mercuric iodide, can be converted into salts containing larger proportions of mercuric iodide by interaction with mercuric iodide, or, alternatively, by the application of heat, triethylsulphonium iodide then being expelled. By using acetone, acetone containing ethyl alcohol, or mixtures of acetone, ethyl alcohol, and water as reaction media, the three double salts described can readily be isolated. Other double salts containing the triethylsulphonium group have been described, *e.g.*, $Et_3SHg_4Cl_9$ (Nasini and Costa, *Gazzetta*, 1891, **21**, 191),

$Et_3SHg_6Br_{13}$ and $Et_3SHg_6Cl_{13}$ (Stromholm, *Ber.*, 1898, **31**, 2285; Hofmann and Rabe, *Z. anorg. Chem.*, 1898, **17**, 26).

Similar methods have been applied to the preparation of double salts of phenyldiethylsulphonium iodide and mercuric iodide and three members of this series have been isolated, *phenyldiethylsulphonium mercuritri-iodide* (VII), *phenyldiethylsulphonium trimercurioctaiodide* (VIII), and *phenyldiethylsulphonium mercuritetraiodide* (IX).



The double salt with the composition $PhSEt_2Hg_2I_5$ is too unstable to be isolated in a state of purity.

Pope and Neville (*loc. cit.*) prepared the mercuritri-iodide of *dl*-phenacylmethylethylsulphonium iodide by using " a concentrated solution of mercuric iodide (one molecular proportion) in aqueous potassium iodide." It would appear from the description that an indefinite amount of potassium iodide was used. The experimental results described above emphasise that the amount of potassium iodide employed determines to a great extent the nature of the double salt obtained, since it competes with the sulphonium iodide for possession of the mercuric iodide. For example, in both the triethylsulphonium and the phenyldiethylsulphonium series of salts the use of excess of potassium iodide results in the formation of the salt with the smallest proportion of mercuric iodide, namely, $(R_3S)_2HgI_4$.

As is indicated in the reaction diagrams, the action of heat on the mercuri-iodides has been investigated. Triethylsulphonium mercuritri-iodide (IV), m. p. 112°, can be heated at 165° without undergoing any profound change. Mercuric iodide separates from acetone solutions of triethylsulphonium dimercuripentaiodide (V), but, since the mercuritri-iodide (I) is produced, no further change occurs. In this respect it resembles the corresponding cæsium compound, $CsHg_2I_5$ (Wells, *loc. cit.*). There is evidence that triethylsulphonium mercuritetraiodide (VI) dissociates in boiling acetone solution into the mercuritri-iodide and the sulphonium iodide, and when heated at its m. p. (151°) it decomposes smoothly, losing a molecular quantity of triethylsulphonium iodide (as a mixture of ethyl iodide and ethyl sulphide), and leaves a residue of the pure mercuritri-iodide.

The greater instability towards heat of the mercuritetraiodide (VI) as compared with the mercuritri-iodide (IV) is doubtless connected with the greater instability of HgI_4^{--} as compared with HgI_3^-. There are apparently other factors influencing the stability of mercuri-iodides which are illustrated by the behaviour of the mercuri-iodides derived from phenyldiethylsulphonium iodide. The mercuritri-iodide (VII) of this series, in marked contrast to triethylsulphonium mercuritri-iodide, decomposes when heated, evolves a molecular proportion of sulphonium iodide, and leaves a stable residue in which two molecules of sulphonium iodide are in combination with three molecules of mercuric iodide. Presumably, therefore, the presence of the phenyl group can cause the sulphonium ion itself to initiate the decomposition. The stability of the product of this change, the trimercurioctaiodide (VIII), is remarkable: it can be heated at 180° for 2 hours without suffering any loss in weight.

EXPERIMENTAL.

Triethylsulphonium Mercuritri-iodide (IV).—(i) This salt, m. p. and mixed m. p. 112—113°, crystallised as sulphur-yellow, prismatic rods (6 g.; 85·7%) from the solution obtained by adding mercuric iodide (4·5 g.; 1 mol.) to a suspension of triethylsulphonium iodide (2·5 g.) in warm acetone (20 c.c.) (Found: C, 10·5; H, 2·2; Hg, 28·4. Calc. for $C_6H_{15}I_3SHg$: C, 10·3; H, 2·1; Hg, 28·5%).

(ii) A clear yellow solution was obtained by adding mercuric iodide (1·13 g.; 1 mol.) to a suspension of triethylsulphonium mercuritetraiodide (2·37 g.; 1 mol.) in acetone (15 c.c.). When the solution had evaporated at the ordinary temperature to 5 c.c., triethylsulphonium mercuritri-iodide (3·10 g.; 89·4% calc.), m. p. 113°, crystallised.

(iii) When a solution of mercuric iodide (9·1 g.) in aqueous potassium iodide (12 c.c.) was added to triethylsulphonium iodide (5 g.) in water (50 c.c.), a slight evolution of heat occurred and triethylsulphonium mercuritri-iodide (14 g.) separated; after crystallisation from ethyl alcohol (400 c.c.), 12·4 g. were obtained, m. p. and mixed m. p. 113—114°.

(iv) Mercuric iodide (45·4 g.) was added to a solution of ethyl sulphide (9·0 g.) in acetone (10 c.c.) and, when no more mercuric iodide would dissolve, even on heating, ethyl iodide (9·0 c.c.) was added. The mixture was heated for 3 minutes; a vigorous reaction then occurred and the clear solution boiled. On cooling, triethylsulphonium mercuritri-iodide (68·5 g.), m. p. 105—110°, separated;

and after recrystallisation from acetone (45 c.c.) 60 g. were obtained, m. p. and mixed m. p. 112—113°.

Triethylsulphonium Dimercuripentaiodide (V).—(i) Mercuric iodide (9·1 g.; 2 mols.) was added to a suspension of triethylsulphonium iodide (2·5 g.) in hot acetone (50 c.c.). On cooling, the resulting clear solution deposited sulphur-yellow needles of triethylsulphonium dimercuripentaiodide (8·8 g.), m. p. 121—122° (Found: Hg, 34·5. Calc. for $C_6H_{15}I_5SHg_2$: Hg, 34·7%).

(ii) To a solution of triethylsulphonium mercuritri-iodide (2·0 g.) in hot acetone (10 c.c.), mercuric iodide (1·3 g.; 1 mol.) was added. The solution, on standing, deposited triethylsulphonium dimercuripentaiodide (3·05 g.; 93% calc.), m. p. and mixed m. p. 121—122°.

(iii) A solution of triethylsulphonium iodide (7·0 g.) in warm acetone (40 c.c.) was saturated with mercuric iodide, filtered, and allowed to cool. The dimercuripentaiodide (5·4 g.), m. p. and mixed m. p. 121—122°, separated. The filtrate was saturated with mercuric iodide: a further crop of the dimercuripentaiodide separated, and the new filtrate was treated as before. This process was repeated until no more mercuric iodide could be dissolved in the filtrate obtained: 5·19 g. of mercuric iodide were dissolved and 11·42 g. (99% calc.) of triethylsulphonium dimercuripentaiodide were obtained.

Triethylsulphonium Mercuritetraiodide (VI).—(i) A solution of potassium mercuritri-iodide (3·2 g.) in water (2·5 c.c.) was added to a solution of ethyl sulphide (1·8 g.) and ethyl iodide (3·3 g.) in acetone (8 c.c.). The resulting clear solution, after 10 days, deposited triethylsulphonium mercuritetraiodide (2·1 g.; 90% calc.) as very pale yellow needles, m. p. 150—151° (decomp.) (Found: Hg, 20·9. Calc. for $C_{12}H_{30}I_4S_2Hg$: Hg, 21·2%). This salt is very sparingly soluble in boiling acetone, benzene, or chloroform and only slightly soluble in boiling acetic acid or ethyl alcohol.

(ii) Mercuric iodide (1·13 g.) was added to a hot solution of triethylsulphonium iodide (1·46 g.; 2 mols.) in acetone (25 c.c.). Triethylsulphonium mercuritetraiodide (2·5 g.; 93% calc.), m. p. 151° (decomp.), was obtained.

(iii) Potassium iodide (1·66 g.; 1 mol.) in water (5 c.c.) was added to a solution of triethylsulphonium mercuritri-iodide (7·0 g.) in warm acetone (20 c.c.). The mercuritetraiodide (4·7 g.; 99% calc.), m. p. 150—151° (decomp.), was obtained.

(iv) Triethylsulphonium mercuritetraiodide (8·7 g.; 92% calc.), m. p. 151° (decomp.), was obtained by the addition of a solution of triethylsulphonium mercuritri-iodide (7·0 g.) in hot acetone (25 c.c.) to a solution of triethylsulphonium iodide (2·5 g.) in the same solvent (25 c.c.). This reaction takes place also in aqueous acetone.

(v) Triethylsulphonium dimercuripentaiodide (1·91 g.) was added gradually to a boiling solution of triethylsulphonium iodide (1·48 g.; 3 mols.) in acetone (60 c.c.). The mercuritetraiodide (3·2 g.; 94% calc.), m. p. 151° (decomp.), was obtained.

(vi) To a solution of triethylsulphonium dimercuripentaiodide (6·9 g.) in warm acetone (50 c.c.), a solution of potassium iodide (1·5 g.; 1·5 mols.) in water (40 c.c.) was added. The mercuritetraiodide (0·7 g.; 25% calc.), m. p. 151° (decomp.), crystallised. The low yield obtained is due to the dissociation of triethylsulphonium mercuritetraiodide into triethylsulphonium mercuritri-iodide and triethylsulphonium iodide in warm aqueous acetone.

(vii) When a current of hydrogen sulphide was passed into a warm solution of triethylsulphonium mercuritri-iodide (9·8 g.) in acetone (160 c.c.) containing water (15 c.c.), a black precipitate of mercuric sulphide formed, which, after about 15 minutes, became bright red, having changed to mercuric iodide. After removal of the precipitate (0·85 g.), the filtrate deposited triethylsulphonium mercuritetraiodide (5·9 g.; 89% calc.), m. p. 148—149° (decomp.).

The action of heat on triethylsulphonium mercuritetraiodide. The salt (18·95 g.) was heated at 145—165° for 2 hours; no further reaction then occurred. The residue (14·5 g.) was separated by recrystallisation from acetone into unchanged mercuritetraiodide (1·0 g.) and triethylsulphonium mercuritri-iodide (13 g.). The distillate obtained (3·2 c.c.) was a mixture of ethyl iodide and ethyl sulphide and, after redistillation (b. p. 72—92°), set to a white crystalline mass of triethylsulphonium iodide, m. p. and mixed m. p. 150° (decomp.).

Triethylsulphonium mercuritetraiodide was also converted quantitatively into triethylsulphonium mercuritri-iodide through the loss of ethyl iodide and ethyl sulphide by heating it with water on a steam-bath.

Phenyldiethylsulphonium Mercuritri-iodide (VII).—(i) A mixture of phenyl ethyl sulphide (27·6 g.), mercuric iodide (91·4 g.), and ethyl iodide (32 g.) in acetone (60 c.c.) was gently warmed and shaken until a clear yellow solution was obtained. After remaining for 5 months in an uncorked flask, this deposited *phenyldiethylsulphonium mercuritri-iodide*, which was recrystallised from acetone–ethyl alcohol and obtained as pale yellow, hard, irregular rhombs (141·5 g.; 95% calc.), m. p. 56—57° (Found: Hg, 26·6. $C_{10}H_{15}I_3SHg$ requires Hg, 26·8%).

(ii) On adding mercuric iodide (0·45 g.; 1 mol.) to a suspension of phenyldiethylsulphonium mercuritetraiodide (1·04 g.) in acetone (10 c.c.), a clear yellow solution was obtained, from which, on addition of ethyl alcohol, phenyldiethylsulphonium mercuritri-iodide (1·4 g.), m. p. and mixed m. p. 54—55°, crystallised.

(iii) When phenyldiethylsulphonium mercuritetraiodide (1·04 g.) was warmed with an excess of aqueous potassium mercuritri-iodide, it was converted into phenyldiethylsulphonium mercuritri-iodide (1·3 g.), m. p. and mixed m. p. 53—54°.

Action of heat on phenyldiethylsulphonium mercuritri-iodide. The salt (10·0 g.) was heated at 120—170° until it ceased to effervesce. The residue [8·2 g.; calc. for $(SPhEt_2)_2Hg_3I_8$, 8·7 g.] consisted of phenyldiethylsulphonium trimercurioctaiodide and had m. p. and mixed m. p. 66—67° (see below) after crystallisation from acetone. When heated for 2 hours at 150°, the trimercurioctaiodide darkened, but otherwise remained unchanged. Further heating for 2 hours at 180° caused it to lose 5·7% in weight, but no profound decomposition occurred.

Phenyldiethylsulphonium Trimercurioctaiodide (VIII).—Mercuric iodide (2·27 g.; 0·5 mol.) was dissolved in a solution of phenyldiethylsulphonium mercuritri-iodide (7·48 g.; 1 mol.) in acetone (10 c.c.). When the resulting solution was diluted with alcohol, *phenyldiethylsulphonium trimercurioctaiodide* (9·5 g.), m. p. 65—66°, separated as pale yellow, irregular rhombs (Found: Hg, 30·8. $C_{20}H_{30}I_8S_2Hg_3$ requires Hg, 30·9%).

Phenyldiethylsulphonium Mercuritetraiodide (IX).—(i) Potassium iodide (1·7 g.; 1 mol.) in water (4 c.c.) was added to a solution of phenyldiethylsulphonium mercuritri-iodide (7·5 g.; 2 mols.) in acetone (15 c.c.). *Phenyldiethylsulphonium mercuritetraiodide* (5·1 g.), m. p. 114—115°, separated almost immediately. Owing to its sparing solubility it could not be recrystallised (Found: C, 22·0; H, 2·9; I, 48·8; Hg, 20·3. $C_{20}H_{30}I_4S_2Hg$ requires C, 23·0; H, 2·9; I, 49·0; Hg, 19·2%).

(ii) To a solution of phenyldiethylsulphonium trimercurioctaiodide (15 g.; 1 mol.) in acetone (30 c.c.), potassium iodide (3·3 g.; 2 mols.) in water (7 c.c.) was added. The mercuritetraiodide (7·6 g.), m. p. and mixed m. p. 114—115°, was obtained.

(iii) A current of hydrogen sulphide was passed for 2 hours into a solution of phenyldiethylsulphonium mercuritri-iodide (15 g.) in a mixture of acetone (15 c.c.) and water (5 c.c.). A precipitate of the mercuritetraiodide (10·2 g.) was produced, m. p. and mixed m. p. 114—115°.

(iv) Hydrogen sulphide was passed for 2 hours into a solution of phenyldiethylsulphonium trimercurioctaiodide (7·8 g.) in acetone (50 c.c.). A yellow precipitate of mercuric iodide (0·65 g.) was removed, and the filtrate allowed to evaporate at the ordinary temperature. The mercuritetraiodide (2·55 g.), m. p. 114—115°

(decomp.), crystallised, and, when the mother-liquor was concentrated and diluted with ethyl alcohol, the mercuritri-iodide (2·5 g.), m. p. 53—54°, was also obtained.

Action of heat on phenyldiethylsulphonium mercuritetraiodide. The salt (3·0 g.) was heated at 110—130° until the evolution of ethyl iodide had ceased. The resinous residue was separated by means of ether into phenyl ethyl sulphide (b. p. 202—204°) and crystalline phenyldiethylsulphonium mercuritri-iodide (2·18 g.), m. p. and mixed m. p. 56—57°.

Phenacylmethylethylsulphonium d-*Bromocamphorsulphonate.*—The preparation and resolution of this salt were carried out by Smiles's method (*loc. cit.*). The *dl*-sulphonium bromide obtained from ω-bromoacetophenone (56·1 g.) and methyl ethyl sulphide (21·4 g.) was converted into the *d*-bromocamphorsulphonate, which, when recrystallised from ethyl alcohol, gave *l*-phenacylmethylethylsulphonium *d*-bromocamphorsulphonate (20 g.), m. p. 196°, $[\alpha]_{5893}$ + 46·0°, $[\alpha]_{5461}$ + 59·0° ($c = 1·17$; $l = 2·0$) in water. The specific rotatory power of this *d*-bromocamphorsulphonate altered only by 1·0° when the salt was recrystallised from absolute or aqueous ethyl alcohol. From the filtrate from this *d*-bromocamphorsulphonate, three other crops of the same salt were obtained: (*a*) 10 g., $[\alpha]_{5461}$ + 71·2°; (*b*) 4 g., $[\alpha]_{5461}$ + 61·1°; (*c*) 4 g., $[\alpha]_{5461}$ + 71·2°.

The combined filtrates from the crops of the *l*-sulphonium salt, on standing for 5 weeks, gave no further crystals, and the addition of picric acid caused the deposition of only a small quantity of the *dl*-picrate, m. p. 126°.

In a second and more successful resolution, a solution of *dl*-phenacylmethylethylsulphonium *d*-bromocamphorsulphonate (86 g.) in aqueous ethyl alcohol (90%, 550 c.c.) was concentrated; a crop of the *l*-sulphonium salt separated, which was fractionally recrystallised from the same solvent. The more soluble *d*-sulphonium salt was obtained by evaporating the combined filtrates from the crystallisation of the *l*-sulphonium salt to a small bulk and precipitating the salt with dry ether. The *d*-sulphonium salt obtained was then washed with dry acetone. The specific rotatory powers ($l = 2$, in water) of the crops of *l*- and *d*-sulphonium salt obtained were as follows :—

Crop.	Weight, g.	M. p.	$[\alpha]_{5780}$.	$[\alpha]_{5461}$.	c.
A	10	193°	+48·7°	+58·1°	1·48
B	6	191—192	50·2	58·0	1·52
C	11	184	54·5	64·8	1·55
D	5	185—186	61·4	71·1	1·55
E	2	182—183	63·2	73·2	1·51
F	2	182—183	—	71·4	1·50

Crops A and B were combined and recrystallised from ethyl alcohol. The resulting *l*-phenacylmethylethylsulphonium salt (7·1 g.), m. p. 193°, had $[\alpha]_{5780} + 50{\cdot}5°$, $[\alpha]_{5461} + 58{\cdot}5°$ ($c = 1{\cdot}55, l = 2{\cdot}0$) in water.

The optically purest *l*-sulphonium salt with $[\alpha]_{5893} + 46{\cdot}03°$, $[\alpha]_{5461} + 59{\cdot}0°$ (obtained in the first resolution), gave *l*-phenacylmethylethylsulphonium picrate, m. p. 128°, $[\alpha]_{5461} - 9{\cdot}8°$, and, after recrystallisation from ethyl alcohol, $[\alpha]_{5893} - 11{\cdot}2°$, $[\alpha]_{5461} - 13{\cdot}5°$ in acetone ($c = 1{\cdot}56$, $l = 2{\cdot}0$). Pope and Neville (*loc. cit.*) record $[\alpha]_{5893} + 41{\cdot}1°$ ($c = 1{\cdot}410, l = 2{\cdot}0$) as the rotatory power of the optically pure *l*-sulphonium *d*-bromocamphorsulphonate and $[\alpha]_{5893} - 10{\cdot}0°$ ($c = 1{\cdot}910$, $l = 2{\cdot}0$) as the maximum rotatory power of the *l*-picrate.

In neither the first nor the second resolution could the *d*-sulphonium salt be obtained in any quantity or even optically pure. Crop F (second resolution) approached optical purity : it gave a *d* + *dl*-sulphonium picrate with $[\alpha]_{5780} + 6{\cdot}0°$, $[\alpha]_{5461} + 6{\cdot}6°$ ($c = 1{\cdot}59$; $l = 2{\cdot}0$) in acetone solution.

The Stability of l-*Phenacylmethylethylsulphonium* d-*Bromocamphorsulphonate in Aqueous Solution and of the* l-*Picrate in Acetone Solution.*—An aqueous solution of the *d*-bromocamphorsulphonate had $[\alpha]_{5461} + 58{\cdot}1°$ when freshly prepared, $[\alpha]_{5461} + 59{\cdot}1°$ after 237 hours and also after 1392 hours.

Six months after it had been prepared, a specimen of the *l*-picrate, m. p. 132—133°, $[\alpha]_{5461} - 16{\cdot}8°$ in acetone ($c = 1{\cdot}012$; $l = 2{\cdot}0$), had $[\alpha]_{5461} - 17{\cdot}8°$ ($c = 1{\cdot}570$; $l = 2{\cdot}0$) in acetone. This acetone solution had $[\alpha]_{5461} - 15{\cdot}0°$ after 741 hours and $[\alpha]_{5461} - 13{\cdot}4°$ after 1897 hours.

dl- *and* l-*Phenacylmethylethylsulphonium Mercuritri-iodide* (III).—When the paste obtained by adding a few drops of acetone to *dl*-phenacylmethylethylsulphonium mercuritetraiodide (see below) (2·2 g.; 1 mol.) and mercuric iodide (0·9 g.; 1 mol.) was warmed, a yellow mass was obtained. It was dissolved in cold acetone and when ethyl alcohol was added dl-*phenacylmethylethylsulphonium mercuritri-iodide* (1·2 g.), m. p. 82—83°, separated in small yellow needles (Found: Hg, 25·6. $C_{11}H_{15}OI_3SHg$ requires Hg, 25·8%).

l-*Phenacylmethylethylsulphonium mercuritri-iodide.* (i) To a solution of *l*-phenacylmethylethylsulphonium *d*-bromocamphorsulphonate (2·0 g.; 1 mol.; $[\alpha]_{5461} + 59°$) in water (20 c.c.) was added a solution of potassium mercuritri-iodide (2·5 g.; 1 mol.) in water (3 c.c.). The oil which separated crystallised to a yellow solid (2·7 g.), m. p. 78—80°, $[\alpha]_{5461} - 7{\cdot}2°$ ($c = 1{\cdot}52$, $l = 2{\cdot}0$). When this solid was recrystallised from acetone–aqueous alcohol, l-*phenacyl-*

methylethylsulphonium mercuritri-iodide (2·3 g.), m. p. 81—82°, was obtained (Found: C, 17·2; H, 2·0; I, 49·2; Hg, 25·6. $C_{11}H_{15}OI_3SHg$ requires C, 17·0; H, 1·9; I, 49·1; Hg, 25·8%). It had $[\alpha]_{5780} - 6{\cdot}4°$, $[\alpha]_{5893} - 9{\cdot}1°$, $[\alpha]_{5461} - 10{\cdot}7°$ ($c = 1{\cdot}918$; $l = 2{\cdot}0$) in acetone solution immediately after the solution had been prepared and also after it had stood at the ordinary temperature for 264 hours. The solution was then unchanged in appearance and free from the odour of alkyl sulphides. After 1368 hours and also after 2865 hours this solution had $[\alpha]_{5461} - 5{\cdot}5°$.

(ii) Sufficient acetone was added to freshly prepared *l*-phenacylmethylethylsulphonium mercuritetraiodide (see below) (0·55 g.) and mercuric iodide (0·22 g.; 1 mol.) to form a pasty mass, which, on being warmed, assumed a homogeneous yellow colour. When alcohol was added to a solution of this paste in acetone, *l*-phenacylmethylethylsulphonium mercuritri-iodide (0·7 g.) separated, m. p. 82° alone and when mixed with the *l*-mercuritri-iodide prepared as described above. In acetone solution it had $[\alpha]_{5780} - 6{\cdot}6°$, $[\alpha]_{5461} - 6{\cdot}8°$ ($c = 2{\cdot}36$, $l = 2{\cdot}0$), values which remained unchanged after 93 hours.

The Permanence of the Rotatory Power of l-*Phenacylmethylethylsulphonium Mercuritri-iodide in Acetone containing Methyl Iodide.*—To 19 c.c. of an acetone solution of the *l*-mercuritri-iodide having $[\alpha]_{5780} - 7{\cdot}1°$, $[\alpha]_{5461} - 7{\cdot}9°$ ($c = 2{\cdot}53$, $l = 2{\cdot}0$), which remained unchanged during 20 hours, methyl iodide (1·37 g.; 15·8 mols.) was added. The solution then had $[\alpha]_{5780} - 7{\cdot}9°$, $[\alpha]_{5461} - 8{\cdot}1°$, unchanged after 161 hours; $[\alpha]_{5461} - 6{\cdot}1°$ after 1032 hours; $[\alpha]_{5461} - 5{\cdot}7°$ after 1358 hours; $[\alpha]_{5461} - 4{\cdot}3°$ after 2522 hours.

The Racemisation of l-*Phenacylmethylethylsulphonium Mercuritri-iodide in Acetone.*—(a) *In the presence of potassium iodide.* *l*-Phenacylmethylethylsulphonium mercuritri-iodide (0·614 g., $[\alpha]_{5461} - 7{\cdot}8°$), potassium iodide (0·3 g.; 5 mols.), and water (1 c.c.) were made up to 20 c.c. with acetone. The solution obtained had $[\alpha]_{5461} - 2{\cdot}4°$, and was optically inactive after 15 hours.

(b) *In the presence of* l-*phenacylmethylethylsulphonium mercuritetraiodide.* To a solution of the *l*-mercuritri-iodide (0·3564 g.) in acetone (20 c.c.), the *l*-mercuritetraiodide (0·2266 g.) was added. The resulting solution had $\alpha_{5461} - 0{\cdot}36°$; after 20 hours, $\alpha_{5461} - 0{\cdot}32°$; after 338 hours, $\alpha_{5461} - 0{\cdot}16°$; and after 861 hours was optically inactive. The *l*-mercuritri-iodide used in this experiment had $[\alpha]_{5461} - 8{\cdot}4°$ in acetone solution, changing to $- 6{\cdot}2°$ after 2043 hours.

Action of Heat on l-*Phenacylmethylethylsulphonium Mercuritri-iodide.*—The salt (0·598 g.; $[\alpha]_{5461} - 7{\cdot}8°$) was heated at 100° for 2 hours. It was then black, had an odour resembling that of alkyl sulphides, weighed 0·583 g., and was optically inactive in acetone solution, from which it could not be precipitated by the addition of either ethyl alcohol or ether.

dl- *and* l-*Phenacylmethylethylsulphonium Mercuritetraiodide.*—An oil, which solidified after 12 hours, separated when a solution of potassium mercuritri-iodide (8·2 g.; 2 mols.) in water (10 c.c.) was added to a solution of *dl*-phenacylmethylethylsulphonium bromide (3·6 g.; 1 mol.) in alcohol (10 c.c.). The solid product (4·3 g.) had m. p. 120—130°, and after crystallisation from dry acetone–ether gave dl-*phenacylmethylethylsulphonium mercuritetraiodide* (1·7 g.), m. p. 134° (Found: Hg, 18·3. $C_{22}H_{30}O_2I_4S_2Hg$ requires Hg, 18·2%).

l-*Phenacylmethylethylsulphonium mercuritetraiodide.* (i) *From* l-*phenacylmethylethylsulphonium* d-*bromocamphorsulphonate.* (a) *Using potassium iodide* (2 *mols.*) *and mercuric iodide* (1 *mol.*) *in ethyl-alcoholic solution.* Potassium iodide (2·65 g.; 2 mols.) and mercuric iodide (3·55 g.; 1 mol.) in hot aqueous acetone (15 c.c., containing water, 5 c.c.) was added to a solution of *l*-phenacylmethylethyl sulphonium *d*-bromocamphorsulphonate (2 g.; 1 mol.; $[\alpha]_{5461}$ + 59·0°) in hot alcohol (40 c.c.). When the mixture was cooled, a white crystalline precipitate (1·8 g.), m. p. 118—120°, was obtained, from which, by recrystallisation from acetone–ether, l-*phenacylmethylethylsulphonium mercuritetraiodide* (1·5 g.) was isolated as clusters of minute white needles, m. p. 122—123° (Found: C, 24·1; H, 2·8; I, 46·7; Hg, 17·9. $C_{22}H_{30}O_2S_2I_4Hg$ requires C, 24·1; H, 2·7; I, 46·6; Hg, 18·2%). In acetone solution it had $[\alpha]_{5780}$ — 8·2°, $[\alpha]_{5461}$ — 9·3° ($c = 2·425$; $l = 2·0$) when this solution was first prepared, $[\alpha]_{5780}$ — 2·9°, $[\alpha]_{5461}$ — 3·1° after 72 hours, and $[\alpha]_{5780}$ — 1·6°, $[\alpha]_{5461}$ — 1·7° after 192 hours.

Another specimen of this *l*-mercuritetraiodide (2 g.), prepared by the addition of potassium mercuritri-iodide (9·3 g.; 2 mols.) in hot water (10 c.c.) to a solution of the *d*-bromocamphorsulphonate (3·0 g.; 1 mol.) in alcohol (50 c.c.), after recrystallisation from acetone–ether, had m. p. 122°, and $[\alpha]_{5893}$ — 6·8°, $[\alpha]_{5780}$ — 7·3°, $[\alpha]_{5461}$ — 7·8° in acetone solution ($c = 2·939$; $l = 2·0$). At the end of 19 hours, this solution had $[\alpha]_{5780}$ — 3·9°, $[\alpha]_{5461}$ — 3·9°; after 41 hours, $[\alpha]_{5780}$ — 2·9°, $[\alpha]_{5461}$ — 2·9°; after 91 hours, $[\alpha]_{5780}$ — 2·3°, $[\alpha]_{5461}$ — 2·2°; and after 139 hours it was optically inactive. The solution, which was originally pale yellow, gradually darkened and developed an odour of alkyl sulphide. After 312 hours, it was found to contain free iodine and the gum which remained on evaporation of the solvent had an odour of ω-bromoacetophenone and deposited *dl*-phenacylmethylethylsulphonium mercuritetraiodide (0·07 g.), m. p. 133°, on standing. From these observations it can be concluded that the racemisation of the *l*-mercuritetraiodide is attended by profound decomposition. Even in the solid state the salt is not stable. For instance, a freshly prepared specimen, m. p. 122—123°, had $[\alpha]_{5461}$ — 10·9° ($c = 1·380$; $l = 2$) in acetone; after 2160 hours, this specimen had m. p. 114—122° and $[\alpha]_{5461}$ — 8·4° in acetone ($c = 1·195$; $l = 2·0$); and at the end of 386 hours this solution was optically inactive.

(b) *Using potassium iodide* (2 *mols.*) *and mercuric iodide* (1 *mol.*) *in aqueous solution.* A solution of potassium iodide (1·35 g.; 2 mols.) and mercuric iodide (1·85 g.; 1 mol.) in water (3 c.c.) was added to a solution of the *d*-bromocamphorsulphonate (2·0 g.; 1 mol.) in water (40 c.c.). The precipitated oil slowly formed a paste (2·9 g.) which, by crystallisation from acetone and alcohol, was separated into the *l*-mercuritetraiodide (0·50 g.), m. p. 122—124°, and the *l*-mercuritri-iodide (1·75 g.), m. p. 78—80°, which, after crystallisation from acetone and aqueous alcohol, had m. p. 81—82° and $[\alpha]_{5461}$ — 8·0° ($c = 5·45$; $l = 2·0$) in acetone.

(c) *Using potassium iodide* (5 *mols.*) *and mercuric iodide* (1 *mol.*). To a solution of the *d*-bromocamphorsulphonate ($[\alpha]_{5461}$ + 59·0°; 1·0 g.) in water (30 c.c.), potassium iodide (1·6 g.; 5 mols.) and mercuric iodide (0·9 g.; 1 mol.) in water (5 c.c.) were added. The oil which separated crystallised on standing and, after recrystallisation from acetone–ether, was obtained (0·5 g.) with m. p. 128—130°, a value which is about 6° higher than that of the other preparations of this compound (Found: C, 23·9; H, 2·7; Hg, 18·4%). This specimen of *l*-phenacylmethylethylsulphonium mercuritetraiodide had $[\alpha]_{5780}$ — 7·6°, $[\alpha]_{5461}$ — 7·9° in acetone solution ($c = 1·32$; $l = 2·0$). After 72 hours this solution had $[\alpha]_{5780}$ and $[\alpha]_{5461}$ — 4·9°, and after 163 hours it was optically inactive.

(ii) *From* l-*phenacylmethylethylsulphonium mercuritri-iodide.* When the solution obtained by mixing a hot acetone solution (5 c.c.) of the *l*-mercuritri-iodide (0·77 g.; $[\alpha]_{5461}$ — 7·9°) with an aqueous solution (2 c.c.) of potassium iodide (0·16 g.; 1 mol.) was cooled, *l*-phenacylmethylethylsulphonium mercuritetraiodide (0·52 g.) crystallised, m. p. 122° alone or when mixed with the compound described under (i). It had $[\alpha]_{5780}$ — 10·9°, $[\alpha]_{5461}$ — 10·9° in acetone solution ($c = 1·38$; $l = 2·0$).

(iii) *By the action of hydrogen sulphide on* l-*phenacylmethylethylsulphonium mercuritri-iodide.* When a current of hydrogen sulphide was passed through a solution of *l*-phenacylmethylethylsulphonium mercuritri-iodide (1·0 g.; $[\alpha]_{5461}$ — 7·8°) in acetone (10 c.c.), mercuric sulphide was precipitated which changed to mercuric iodide after 12 hours. The filtrate from this precipitate, when diluted with ether, gave *l*-phenacylmethylethylsulphonium mercuritetraiodide, m. p. and mixed m. p. 122°. It had $[\alpha]_{5461}$ − 9·7° (c = 1·86; l = 2·0) in acetone.

The Racemisation of l-*Phenacylmethylethylsulphonium Mercuritetraiodide in Acetone containing Methyl Iodide.*—To 20 c.c. of the acetone solution of l-phenacylmethylethylsulphonium mercuritetraiodide ($[\alpha]_{5461}$ − 10·9°; see above), methyl iodide (0·23 g.; 4·5 mols.) was added. The freshly prepared solution had $[\alpha]_{5780}$ − 11·3°, $[\alpha]_{5461}$ − 11·3°; after 19 hours, $[\alpha]_{5780}$ and $[\alpha]_{5461}$ − 4·7°; after 42 hours, it was optically inactive. This solution, in contrast to the similar solution containing the l-mercuritri-iodide described above, did not change in appearance, and even after 120 hours it was still pale yellow and free from the odour of alkyl sulphides.

The Action of Heat on l-*Phenacylmethylethylsulphonium Mercuritetraiodide.*—The salt (0·611 g.; $[\alpha]_{5461}$ − 10·5°), when heated for a few minutes, turned black and developed a strong odour resembling that of alkyl sulphides. After 2 hours' heating, the black residue weighed 0·582 g. (loss in weight, 4·74%). It was soluble in acetone, giving an optically inactive solution which yielded no solid products when diluted with ethyl alcohol or ether.

l- *and* dl-*Phenacylmethylethylsulphonium Dimercuriheptachloride.*—When potassium mercuritrichloride (2·1 g.; 1 mol.) in water (5 c.c.) was added to a solution of dl-phenacylmethylethylsulphonium d-bromocamphorsulphonate (3 g.; $[\alpha]_{5461}$ + 64·8°) in water (60 c.c.), an oil separated, which crystallised as soft white needles (2·5 g.), m. p. 152—154° (decomp.). After recrystallisation from acetone–ether, these crystals gave dl-*phenacylmethylethylsulphonium dimercuriheptachloride*, m. p. 153° (decomp.) (Found: C, 32·1; H, 3·9; S, 7·7; Cl, 20·7; Hg, 33·3. $C_{33}H_{45}O_3S_3Cl_7Hg_2$ requires C, 32·1; H, 3·7; S, 7·8; Cl, 20·2; Hg, 33·0%).

In two similar experiments, potassium mercuritrichloride (2 mols.) being used in one and potassium chloride (5 mols.) together with mercuric chloride (1 mol.) in the other, 2·0 g. and 1·5 g. respectively of the dl-dimercuriheptachloride were obtained.

l-*Phenacylmethylethylsulphonium dimercuriheptachloride*, m. p. 153°, was prepared from the d-bromocamphorsulphonate of the l-sulphonium base (1·0 g.; $[\alpha]_{5461}$ + 59·0°) and potassium mercuritrichloride (0·7 g.; 1 mol.) in water (35 c.c.) (Found: Hg, 33·0%). It is insoluble in water, ethyl alcohol and ether and slightly soluble in acetone, but more soluble in methyl alcohol. It had $[\alpha]_{5780}$ − 10·7°, $[\alpha]_{5461}$ − 11·3° in methyl-alcoholic solution (c = 1·17; l = 2·0). After 1947 hours this solution had $[\alpha]_{5780}$ and $[\alpha]_{5461}$ − 7·7°.

dl- *and* l-*Phenacylmethylethylsulphonium Cadmitetraiodides.*—dl-*Phenacylmethylethylsulphonium cadmitetraiodide.* (a) *Using potassium iodide* (1 *mol.*) *and cadmium iodide* (1 *mol.*). To a solution of phenacylmethylethylsulphonium bromide (5·4 g.) in alcohol (10 c.c.), cadmium iodide (7·43 g.; 1 mol.) and potassium iodide (3·38 g.; 1 mol.) in water (4·5 c.c.) were added. A brown pasty solid was precipitated which, by crystallisation from acetone–alcohol, yielded dl-*phenacylmethylethylsulphonium cadmitetraiodide* as a white powder (2·8 g.), m. p. 126° (Found: Cd, 10·8. $C_{22}H_{30}O_2I_4S_2Cd$ requires Cd, 11·1%).

(b) *Using potassium iodide* (2 *mols.*) *and cadmium iodide* (1 *mol.*). A solution of cadmium iodide (7·43 g.; 1 mol.) and potassium iodide (6·76 g.; 2 mols.) in water (10 c.c.) was used in place of the solution described above. A precipitate (9·8 g.), m. p. 115—125°, was obtained which, recrystallised from anhydrous acetone–ether, gave the *dl*-cadmitetraiodide (7·7 g.), m. p. 126° (Found: Cd, 10·8%).

l-*Phenacylmethylethylsulphonium cadmitetraiodide.* To a solution of *l*-phenacylmethylethylsulphonium *d*-bromocamphorsulphonate, $[\alpha]_{5461}$ + 59·0°, (2·0 g.) in hot alcohol (40 c.c.), potassium cadmitetraiodide (2·8 g.; 1 mol.) in aqueous acetone (acetone 10 c.c. + water 5 c.c.) was added. After 24 hours, a mass of needles, m. p. 133°, separated which, after recrystallisation from acetone and ether, weighed 1·0 g. and had m. p. 132—133° (Found: Cd, 10·9%).

l-*Phenacylmethylethylsulphonium cadmitetraiodide* had $[\alpha]_{5780}$ − 9·9°, $[\alpha]_{5461}$ − 10·2° in acetone ($c = 1{\cdot}41$; $l = 2{\cdot}0$); this solution had $[\alpha]_{5780}$ and $[\alpha]_{5461}$ − 3·5° after 72 hours and was optically inactive after 164 hours.

dl-*Phenacylmethylethylsulphonium Cadmipentaiodide*,

$$[COPh{\cdot}CH_2{\cdot}SMeEt]_3CdI_5.$$

—This compound was obtained by using the method previously employed for the preparation of mercuritri-iodides.

dl-Phenacylmethylethylsulphonium cadmitetraiodide (1·0 g.) and cadmium iodide (0·35 g.; 1 mol.) were warmed together with sufficient dry acetone to form a paste, from which the acetone was subsequently removed by distillation on a steam-bath. The hard, white, crystalline material obtained was dissolved in acetone, from which it was precipitated by addition of alcohol. It (1·1 g.) then had m. p. 130—132° and, by recrystallisation from acetone–alcohol, dl-*phenacylmethylethylsulphonium cadmipentaiodide* was obtained as white needles, m. p. 134—136° (Found: S, 7·4; Cd, 8·6. $C_{33}H_{45}O_3I_5S_3Cd$ requires S, 7·2; Cd, 8·5%).

l-*Phenacylmethylethylsulphonium Cadmipentaiodide.*—From *l*-phenacylmethylethylsulphonium cadmitetraiodide (2·0 g.; 1 mol.; $[\alpha]_{5461}$ − 10·2°) and cadmium iodide (0·35 g.; 1 mol.), by the method described above, l-*phenacylmethylethylsulphonium cadmipentaiodide* (0·5 g.), m. p. 128°, was obtained (Found: Cd, 8·7%). It had $[\alpha]_{5780}$ and $[\alpha]_{5461}$ − 9·0° in acetone ($c = 1{\cdot}115$; $l = 2{\cdot}0$).

After 25 hours this solution had $[\alpha]_{5780}$ and $[\alpha]_{5461}$ — 5·4° and after 48 hours it was optically inactive.

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