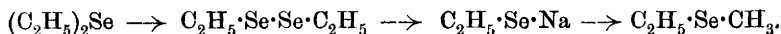


CLV.—*Asymmetric Optically Active Selenium Compounds and the Sexavalency of Selenium and Sulphur. d- and l-Phenylmethylselenetine Salts.*

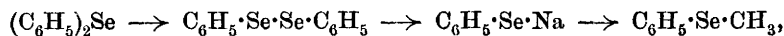
By WILLIAM JACKSON POPE, F.R.S., and ALLEN NEVILLE, B.Sc.

THE fact that amorphous substances can exhibit optical activity as a result of the presence in the molecule of asymmetric atoms other than those of carbon having been placed beyond question by the work of Pope, Peachey, and Harvey (Trans., 1899, 75, 1127; 1900, 77, 1072; 1901, 79, 828), it is important that the results obtained by these authors should be extended to compounds of as large a number of elements as possible, as the foundation would thus be laid for a general stereochemical scheme which would embrace all the elements. For this reason, we have investigated substances containing an asymmetric quadrivalent selenium atom and, in the present paper, contribute results proving that such an atom has a tetrahedral environment and gives rise to optical activity.

For the purposes of this investigation a mixed alkyl selenide was naturally required, and, methods for the preparation of such substances not having been previously devised, it was proposed to prepare methyl ethyl selenide by a series of steps sufficiently indicated by the following scheme:



Although we proceeded far enough with this course to ascertain definitely that it would lead to success, it was found that the manipulation of large quantities of the volatile diethyl diselenide, unless performed with irksome precautions, gave rise to unpleasant physiological symptoms in the operator; this plan of attack was therefore abandoned in favour of one based on the following considerations. The difficulties encountered in dealing with the dialkyl selenides are due to their volatility and might be avoided by the use of a selenide of high molecular weight, provided that such a substance had, in other respects, the necessary properties; that is to say, if phenyl methyl selenide, prepared by the following series of steps:



would combine with bromoacetic acid to give a stable selenetine of the constitution  $C_6H_5 \cdot Se \begin{matrix} CH_3 \\ \searrow \\ CH_2 \cdot CO_2H \end{matrix} \begin{matrix} Br \\ \nearrow \end{matrix}$ , the desired object would be attained. Although phenyl methyl sulphide is quite inert towards bromoacetic acid, it was thought probable that, since the oxygen

in alkyl oxides exhibits more reluctance than the sulphur in alkyl sulphides to become quadrivalent, the selenium in alkyl selenides might have so great a tendency to become quadrivalent as to counteract the inhibiting influence of a phenyl group and so cause phenyl methyl selenide to combine readily with bromoacetic acid. This surmise proved correct, and a striking illustration is thus furnished of the periodic gradation in the ease with which bivalent oxygen, sulphur, and selenium become quadrivalent.

The only selenetine previously described is that prepared from diethyl selenide and bromoacetic acid by Carrara (*Gazzetta*, 1894, 24, ii, 173); this author, however, gives no data from which an opinion can be formed as to the relative stability of the thetines and selenetines. It is important to note in this connection that whilst an aqueous solution of diethylthetine bromide evolves a strong odour of ethyl sulphide during evaporation on the water-bath, phenylmethylselenetine bromide remains practically odourless under similar conditions; although the latter substance contains the highly acidic phenyl group, the basic character of the quadrivalent selenium atom imparts great stability to the selenetine.

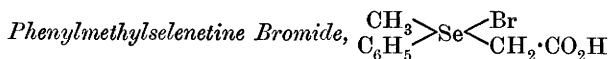
*Phenyl Methyl Selenide, C<sub>6</sub>H<sub>5</sub>·Se·CH<sub>3</sub>.*

Diphenylsulphone is converted into diphenyl selenide and the latter into diphenyl diselenide by the convenient method given by Krafft and Lyons (*Ber.*, 1894, 27, 1761); the diselenide (1 mol.) is converted into sodiophenyl selenide by adding sodium wire to its absolute alcoholic solution and, on running in methyl iodide (2 mols.), vigorous action ensues with formation of phenyl methyl selenide and separation of sodium iodide. After distilling off most of the alcohol, treating with water, and extracting with ether, the ethereal solution is dried over potash and distilled; a good yield of phenyl methyl selenide is obtained as a pale yellow oil which boils at 200—201° without decomposition, and has a not unpleasant aromatic, garlic-like odour:

0.1623 gave 0.2922 CO<sub>2</sub> and 0.0684 H<sub>2</sub>O. C = 49.04; H = 4.68.

C<sub>7</sub>H<sub>8</sub>Se requires C = 49.12; H = 4.67 per cent.

Phenyl methyl selenide is the first mixed alkyl selenide which has been described, and seems to be much more stable in the air than the phenyl hydrogen selenide prepared by Krafft and Lyons (*loc. cit.*).



On warming a mixture of phenyl methyl selenide and bromoacetic acid in molecular proportion on the water-bath, combination takes

place rapidly with development of heat and formation of a white, crystalline mass; after crystallisation from a mixture of ether and alcohol, the selenetine bromide is obtained in white, crystalline scales melting at  $111^{\circ}$ . It is very soluble in water or alcohol, but practically insoluble in ether:

0.1554 gave 0.1985  $\text{CO}_2$  and 0.0504  $\text{H}_2\text{O}$ .  $\text{C} = 34.81$ ;  $\text{H} = 3.60$ .

0.3400 „ 0.08772 Br with standard  $\text{AgNO}_3$ .  $\text{Br} = 25.80$ .

$\text{C}_9\text{H}_{11}\text{O}_2\text{BrSe}$  requires  $\text{C} = 34.83$ ;  $\text{H} = 3.54$ ;  $\text{Br} = 25.81$  per cent.

*Resolution of Externally Compensated Phenylmethylselenetine Bromide.*

On exactly precipitating externally compensated phenylmethylselenetine bromide with silver *d*-bromocamphorsulphonate in hot aqueous solution, filtering off the silver bromide and evaporating the filtrate to dryness, a white, crystalline residue is obtained; this is systematically fractionally crystallised from absolute alcohol, the less soluble fractions being passed in one direction through a series of beakers, whilst the more soluble portions proceed in the opposite direction. The least soluble constituent is *d*-phenylmethylselenetine *d*-bromocamphorsulphonate (*d*-B, *d*-A), and separates from alcohol in small, colourless, rectangular tablets melting at  $168^{\circ}$ . The crystals apparently belong to the orthorhombic system and exhibit the forms {001}, {101}, and {011}; the form {001} is predominant, the *c*-axis is the acute bisectrix, and the optic axial plane is  $a(100)$ . The optic axial angle is large, and the double refraction is positive in sign:

0.1511 gave 0.2336  $\text{CO}_2$  and 0.0630  $\text{H}_2\text{O}$ .  $\text{C} = 42.15$ ;  $\text{H} = 4.63$ .

$\text{C}_{19}\text{H}_{25}\text{O}_6\text{BrSSe}$  requires  $\text{C} = 42.22$ ;  $\text{H} = 4.62$  per cent.

The proof of the purity of the salt and the final determination of its optical constants are given by the following measurements of the rotatory powers of three consecutive fractions obtained on crystallising it from alcohol:

(1) 0.2216 gram, made up to 25 c.c. with water, gave  $\alpha_D + 1.09^{\circ}$  in a 2 dm. tube; whence  $[\alpha]_D + 61.5^{\circ}$  and  $[M]_D + 332.0^{\circ}$ .

(2) 0.2528 gram, made up to 25 c.c. with water, gave  $\alpha_D + 1.24^{\circ}$  in a 2 dm. tube; whence  $[\alpha]_D + 61.3^{\circ}$  and  $[M]_D + 331.1^{\circ}$ .

(3) 0.2356 gram, made up to 25 c.c. with water, gave  $\alpha_D + 1.15^{\circ}$  in a 2 dm. tube; whence  $[\alpha]_D + 61.0^{\circ}$  and  $[M]_D + 329.5^{\circ}$ .

The mean values  $[\alpha]_D + 61.26^{\circ}$  and  $[M]_D + 330.8^{\circ}$  are thus obtained, and since the molecular rotatory power of the *d*-bromocamphorsulphonic ion in aqueous solution is  $[M]_D + 270.0^{\circ}$ , it follows that the corresponding value for the *d*-phenylmethylselenetine ion is  $[M]_D + 60.8^{\circ}$ .

After separating the *d*-phenylmethylselenetine *d*-bromocamphorsulphonate as far as possible, there remains a very soluble residue which has a tendency to become gummy, but by repeated crystallisation from water, *l*-phenylmethylselenetine *d*-bromocamphorsulphonate is obtained in minute, white scales. It is finally purified by crystallisation from alcohol, and forms aggregates of colourless needles melting at  $151^{\circ}$  :

0.1613 gave 0.2493  $\text{CO}_2$  and 0.0671  $\text{H}_2\text{O}$ .  $\text{C} = 42.09$  ;  $\text{H} = 4.58$ .

$\text{C}_{19}\text{H}_{25}\text{O}_6\text{BrSSe}$  requires  $\text{C} = 42.22$  ;  $\text{H} = 4.62$  per cent.

The purity of this material was proved, and its rotatory constants were ascertained, by the following determinations of the rotatory power of three consecutive fractions :

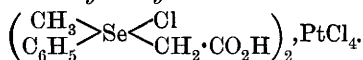
(1) 0.2461 gram, made up to 25 c.c. with water, gave  $\alpha_D + 0.76^{\circ}$  in a 2 dm. tube ; whence  $[\alpha]_D + 38.6^{\circ}$  and  $[\text{M}]_D + 208.4^{\circ}$ .

(2) 0.2371 gram, made up to 25 c.c. with water, gave  $\alpha_D + 0.74^{\circ}$  in a 2 dm. tube ; whence  $[\alpha]_D + 39.0^{\circ}$  and  $[\text{M}]_D + 210.7^{\circ}$ .

(3) 0.2511 gram, made up to 25 c.c. with water, gave  $\alpha_D + 0.78^{\circ}$  in a 2 dm. tube ; whence  $[\alpha]_D + 38.8^{\circ}$  and  $[\text{M}]_D + 209.7^{\circ}$ .

The mean values  $[\alpha]_D + 38.81^{\circ}$  and  $[\text{M}]_D + 209.6^{\circ}$  are thus obtained, and, taking  $[\text{M}]_D + 270.0^{\circ}$  for the *d*-bromocamphorsulphonic ion, the molecular rotatory power of the *l*-phenylmethylselenetine ion is calculated as  $[\text{M}]_D - 60.4^{\circ}$ , a number which agrees very closely with the value  $[\text{M}]_D + 60.8^{\circ}$  obtained above for the enantiomorphously related ion.

*d*- and *l*-Phenylmethylselenetine Platinichlorides,



On adding a cold alcoholic solution of platinic chloride to an alcoholic solution of either of the above *d*-bromocamphorsulphonates containing a little hydrochloric acid, the corresponding platinichloride slowly separates as a microcrystalline, yellow powder ; the platinichlorides are insoluble in water or alcohol, but very soluble in acetone, and crystallise from a hot mixture of acetone and water in minute, yellow prisms melting at  $171^{\circ}$ . The first of the appended analyses was made on *d*-phenylmethylselenetine platinichloride, and the second on its enantiomorphously related isomeride :

(1) 0.1835 gave 0.1672  $\text{CO}_2$  and 0.0414  $\text{H}_2\text{O}$ .  $\text{C} = 24.85$  ;  $\text{H} = 2.50$ .

(2) 0.1923 „ 0.1752  $\text{CO}_2$  „ 0.0432  $\text{H}_2\text{O}$ .  $\text{C} = 24.80$  ;  $\text{H} = 2.49$ .

$\text{C}_{18}\text{H}_{22}\text{O}_4\text{Cl}_6\text{PtSe}_2$  requires  $\text{C} = 24.88$  ;  $\text{H} = 2.53$  per cent.

Three successive fractions from the crystallisation of the *d*-platinichloride gave the following determinations of rotatory power :

(1) 0.5124 gram, made up to 25 c.c. with acetone, gave  $\alpha_D + 0.26^\circ$  in a 2 dcm. tube; whence  $[\alpha]_D + 6.3^\circ$  and  $[M]_D + 55.0^\circ$ .

(2) 0.5561 gram, made up to 25 c.c. with acetone, gave  $\alpha_D + 0.28^\circ$  in a 2 dcm. tube; whence  $[\alpha]_D + 6.3^\circ$  and  $[M]_D + 54.6^\circ$ .

(3) 0.5474 gram, made up to 25 c.c. with acetone, gave  $\alpha_D + 0.28^\circ$  in a 2 dcm. tube; whence  $[\alpha]_D + 6.4^\circ$  and  $[M]_D + 55.5^\circ$ .

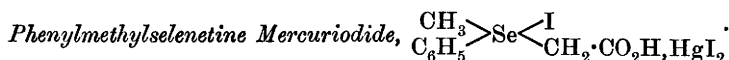
The mean values are thus  $[\alpha]_D + 6.34^\circ$  and  $[M]_D + 55.0^\circ$ . A similar set of three values were also obtained from consecutive fractions of the enantiomorphously related isomeride.

(1) 0.6124 gram, made up to 25 c.c. with acetone, gave  $\alpha_D - 0.31^\circ$  in a 2 dcm. tube; whence  $[\alpha]_D - 6.3^\circ$  and  $[M]_D - 54.8^\circ$ .

(2) 0.5225 gram, made up to 25 c.c. with acetone, gave  $\alpha_D - 0.26^\circ$  in a 2 dcm. tube; whence  $[\alpha]_D - 6.2^\circ$  and  $[M]_D - 54.0^\circ$ .

(3) 0.4812 gram, made up to 25 c.c. with acetone, gave  $\alpha_D - 0.24^\circ$  in a 2 dcm. tube; whence  $[\alpha]_D - 6.2^\circ$  and  $[M]_D - 54.1^\circ$ .

The mean values, namely,  $[\alpha]_D - 6.25^\circ$  and  $[M]_D - 54.3^\circ$ , are in close numerical agreement with those obtained for the enantiomorphously related isomeride. The preparation in a pure state of these optically active platinichlorides containing no asymmetric carbon atoms completes the proof that the presence of an asymmetric quadrivalent selenium atom causes optical activity.



On adding a concentrated aqueous potassium iodide solution of mercuric iodide (1 mol.) to one of either *d*- or *l*-phenylmethylselenetine *d*-bromocamphorsulphonate or of externally compensated phenylmethylselenetine bromide (1 mol.), the optically inactive mercuriodide separates quantitatively as a flocculent, white powder; after crystallisation from dilute alcohol, it is obtained in colourless, crystalline scales melting at  $141\text{--}142^\circ$ . The substance is freely soluble in acetone, less so in alcohol and practically insoluble in water or ether.

The polarimetric examination of this salt in acetone solution showed it to be optically inactive although prepared from a salt of the pure optically active selenetine, and on making a number of preparations of the mercuriodide from *d*- and *l*-phenylmethylselenetine *d*-bromocamphorsulphonate and from the externally compensated bromide, it was found that the same substance is produced from each of these three materials; the salts from the three sources are optically inactive, have the same microcrystalline properties, and no change of melting point results on mixing any two of them.

This result is a very remarkable one, because Pope and Harvey

showed (*loc. cit.*) that no optical inversion attends the formation of *d*- or *l*-benzylphenylallylmethylammonium mercuriodide from its constituent salts, and Pope and Peachey (Trans., 1900, '77, 1072) showed that no racemisation takes place during the formation of *d*-methylethylthetine platinichloride, whilst in the present paper it is shown that the *d*- and *l*-phenylmethylselenetine platinichlorides are still optically active; optical inversion therefore is not an invariable accompaniment to the formation of a double salt or salt of a complex acid. In order to preclude the possibility that the selenetine mercuriodides described above are really optically active, but have very small specific rotatory powers and as the observation of the racemisation of the mercuriodides should have important bearings on the constitution of such substances and on the valency of sulphur and selenium, it seemed desirable to prepare and examine the mercuriodides of an optically active sulphonium base.

For this purpose, we selected the *d*- and *l*-methylethylphenacylthetine *d*-bromocamphorsulphonates prepared by Smiles (Trans., 1900, '77, 1174) rather than the *d*-methylethylthetine *d*-bromocamphorsulphonate previously described by Pope and Peachey (*loc. cit.*), considering the higher rotatory powers exhibited by the former substances as likely to facilitate the investigation. On repeating Smiles's work, much higher values were obtained for the rotation constants than were given by him, and it is hence to be concluded that he did not succeed in obtaining the active thetine salts in a state of purity.

We find that *l*-methylethylphenacylthetine *d*-bromocamphorsulphonate melts at 196°, and four consecutive fractions of the carefully purified salt gave the following determinations of rotatory power :

- (1) 0.3545 gram, made up to 25 c.c. with water, gave  $\alpha_D + 1^\circ 10'$  in a 2 dcm. tube; whence  $[\alpha]_D + 41.1^\circ$  and  $[M]_D + 207.6^\circ$ .
- (2) 0.4288 gram, made up to 25 c.c. with water, gave  $\alpha_D + 1^\circ 26'$  in a 2 dcm. tube; whence  $[\alpha]_D + 41.8^\circ$  and  $[M]_D + 210.9^\circ$ .
- (3) 0.3836 gram, made up to 25 c.c. with water, gave  $\alpha_D + 1^\circ 18'$  in a 2 dcm. tube; whence  $[\alpha]_D + 42.4^\circ$  and  $[M]_D + 213.9^\circ$ .
- (4) 0.4109 gram, made up to 25 c.c. with water, gave  $\alpha_D + 1^\circ 22'$  in a 2 dcm. tube; whence  $[\alpha]_D + 41.5^\circ$  and  $[M]_D + 209.8^\circ$ .

The mean values for the salt are  $[\alpha]_D + 41.7^\circ$  and  $[M]_D + 210.6^\circ$ .

*d*-Methylethylphenacylthetine *d*-bromocamphorsulphonate melts at 180—181° and two consecutive fractions of the salt gave the following results :

- (1) 0.4714 gram, made up to 25 c.c. with water, gave  $\alpha_D + 2^\circ 29'$  in a 2 dcm. tube; whence  $[\alpha]_D + 65.8^\circ$  and  $[M]_D + 332.5^\circ$ .
- (2) 0.3525 gram, made up to 25 c.c. with water, gave  $\alpha_D + 1^\circ 52'$  in a 2 dcm. tube; whence  $[\alpha]_D + 66.0^\circ$  and  $[M]_D + 333.2^\circ$ .

The mean values are thus  $[\alpha]_D + 65.9^\circ$  and  $[M]_D + 332.8^\circ$ .

The molecular rotatory power of the optically active methylethylphenacylthetine ion in aqueous solution, calculated as one-half the difference of the values for the *d*-bromocamphorsulphonate of the *d*- and *l*-bases, is thus:  $[M]_D = \pm (332.8/2 - 210.6/2) = \pm 61.1^\circ$ ; the value calculated from Smiles's results, namely,  $[M]_D \pm 19.4^\circ$ , is less than one-third of this.

The *d*- and *l*-methylethylphenacylthetine picrates, prepared from the corresponding *d*-bromocamphorsulphonates, were fractionally crystallised from acetone and the rotatory powers of two successive fractions of each determined with the following results:

*d*-Methylethylphenacylthetine Picrate.

(1) 0.4512 gram, made up to 25 c.c. with acetone, gave  $\alpha_D + 0^\circ 21'$  in a 2 dm. tube; whence  $[\alpha]_D + 9.7^\circ$  and  $[M]_D + 41.3^\circ$ .

0.5121 gram, made up to 25 c.c. with alcohol, gave  $\alpha_D + 0^\circ 20'$  in a 2 dm. tube; whence  $[\alpha]_D + 8.1^\circ$  and  $[M]_D + 34.6^\circ$ .

(2) 0.3912 gram, made up to 25 c.c. with acetone, gave  $\alpha_D + 0^\circ 18'$  in a 2 dm. tube; whence  $[\alpha]_D + 9.6^\circ$  and  $[M]_D + 40.8^\circ$ .

0.4411 gram, made up to 25 c.c. with alcohol, gave  $\alpha_D + 0^\circ 17'$  in a 2 dm. tube; whence  $[\alpha]_D + 8.0^\circ$  and  $[M]_D + 34.2^\circ$ .

*l*-Methylethylphenacylthetine Picrate.

(1) 0.4912 gram, made up to 25 c.c. with acetone, gave  $\alpha_D - 0^\circ 23'$  in a 2 dm. tube; whence  $[\alpha]_D - 9.7^\circ$  and  $[M]_D - 41.5^\circ$ .

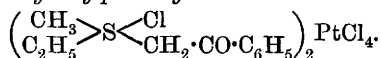
0.4512 gram made up to 25 c.c. with alcohol, gave  $\alpha_D - 0^\circ 18'$  in a 2 dm. tube; whence  $[\alpha]_D - 8.3^\circ$  and  $[M]_D - 35.4^\circ$ .

(2) 0.4775 gram, made up to 25 c.c. with acetone, gave  $\alpha_D - 0^\circ 23'$  in a 2 dm. tube; whence  $[\alpha]_D - 10.0^\circ$  and  $[M]_D - 42.7^\circ$ .

0.4621 gram, made up to 25 c.c. with alcohol, gave  $\alpha_D - 0^\circ 19'$  in a 2 dm. tube; whence  $[\alpha]_D - 8.5^\circ$  and  $[M]_D - 36.4^\circ$ .

*d*-Methylethylphenacylthetine picrate thus gave the mean values  $[\alpha]_D + 9.63^\circ$  and  $[M]_D + 41.1^\circ$  in acetone solution, and  $[\alpha]_D + 8.06^\circ$  and  $[M]_D + 34.4^\circ$  in absolute alcoholic solution. The enantiomorphously related salt gives  $[\alpha]_D - 9.88^\circ$  and  $[M]_D - 42.1^\circ$  in acetone and  $[\alpha]_D - 8.42^\circ$  and  $[M]_D - 35.9^\circ$  in alcohol.

*l*-Methylethylphenacylthetine Platinichloride,



This salt is obtained in golden-yellow scales melting at  $184^\circ$ , on crystallising from dilute acetone the precipitate formed on adding

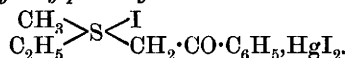
acidified platinic chloride solution to the corresponding *d*-bromocamphorsulphonate; it is very sparingly soluble in the ordinary solvents:

0.2412 gave 0.0584 Pt. Pt = 24.62.

$C_{22}H_{30}O_2Cl_6S_2Pt$  requires Pt = 24.43 per cent.

0.2112 gram, made up to 50 c.c. with concentrated hydrochloric acid, gave  $\alpha_D -0.13^\circ$  in a 4 dm. tube; whence  $[\alpha] -7.7^\circ$  and  $[M]_D -61.4^\circ$ . It is thus evident that the formation of the platini-chloride is not accompanied by optical inversion.

*Methylethylphenacylthetine Mercuriodide,*



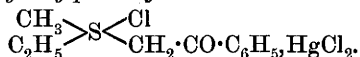
On adding a concentrated solution of mercuric iodide (1 mol.) in aqueous potassium iodide to one of *d*- or *l*-methylethylphenacylthetine *d*-bromocamphorsulphonate or of externally compensated methylethylphenacylthetine bromide (1 mol.), the optically inactive mercuriodide is precipitated. It is insoluble in benzene, ethyl acetate, or water, but crystallises from acetone or dilute alcohol in small, colourless scales melting at  $128^\circ$ . A number of preparations were polarimetrically examined in acetone solution, but all were optically inactive:

0.3256 gave 0.1922  $HgI_2$ .  $HgI_2 = 59.02$ .

0.1615 „ 0.0920  $HgI_2$ .  $HgI_2 = 57.94$ .

$C_{11}H_{15}OI_3SHg$  requires  $HgI_2 = 58.50$  per cent.

*Methylethylphenacylthetine Mercurichloride,*



The optically inactive mercurichloride is prepared by adding an aqueous solution of potassium chloride and mercuric chloride to one of a salt of the *d*-, *l*-, or externally compensated thetine, and crystallising the precipitate from dilute alcohol; it forms glistening, white scales melting at  $119^\circ$ , and is insoluble in water or ether but dissolves in alcohol or acetone. The preparations obtained from the three sources were identical and were optically inactive in acetone solution:

0.2162 gave 0.0464 Cl on titration. Cl = 21.46.

0.3114 „ 0.0669 Cl „ Cl = 21.48.

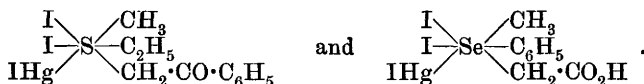
$C_{11}H_{15}OCl_3SHg$  requires Cl = 21.23 per cent.

The fact that methylethylphenylselenetine mercuriodide and methylethylphenacylthetine mercuriodide and mercurichloride are all three obtained as optically inactive substances from salts of the optically active selenetine or thetine must be regarded as proof that optical



inversion actually does take place during their formation, for it can hardly be supposed that the three different substances are really optically active but happen to possess specific rotatory powers so small as to have evaded detection.

The non-occurrence of optical inversion when *d*- and *l*-benzyl-phenylallylmethylammonium salts are converted into their mercuriodides led Pope and Harvey (Trans., 1901, 79, 840) to regard as improbable the suggestion that nitrogen is septavalent in such compounds and also, by analogy, that the sulphur in sulphonium mercuriodides is sexavalent; the facts now brought forward, however, necessitate a revision of this view. If, as was suggested by Smiles for the sulphonium mercuriodides (Trans., 1900, 77, 160), the quadri-valent sulphur or selenium atom in sulphonium or selenonium salts become sexavalent during the formation of the mercuriodides, the latter have the following constitutions:



The simplest environment of the sexavalent atom would be one in which the six atomic groups are situated on three lines drawn at right angles to each other through the sexavalent atom, the six groups being thus situated at the apices of an octahedron of which the sexavalent atom occupies the centre. The most symmetrical manner in which the two new atomic groups can enter the original tetrahedral configuration during its conversion into the octahedral one results in their occupying diametrically opposite vertices of the octahedron, and if this occurs, the four groups *a*, *b*, *c*, and *i*, which are originally tetrahedrally distributed (Fig. 1, p. 1561), necessarily fall into the same plane as the central sulphur or selenium atom at the moment when the two new groups, *i* and *h*, become joined on (Fig. 2).

But as the groups *a*, *b*, *c*, and *i* fall into a plane with the sulphur or selenium atom, the enantiomorphism due to their distribution simultaneously disappears and an optically inactive product would therefore probably result. A less symmetrical method of inserting the two groups, *i* and *h*, in the original compound, which leads, however, to an octahedral configuration of higher symmetry than Fig. 2, is illustrated by Fig. 3; this is a non-enantiomorphous configuration, and if it represents the mercuriodides, the latter would necessarily be optically inactive. The other possible configurations of the sexavalent sulphur or selenium compounds need not be now discussed; in their formation, the groups *h* and *i* require to be inserted in a very unsymmetrical manner and the product would have a highly unsymmetrical configuration. That they should be produced seems improbable in

view of the tendency towards the formation of symmetrical products in chemical reactions.

During the conversion of a quinquevalent into a septavalent nitrogen atom, unless in the resulting substance the original five groups lie in the same plane as the nitrogen atom, there is no reason to expect the five groups to lose their enantiomorphous arrangement or for the two new atomic groups to assume such positions in the

FIG. 1.

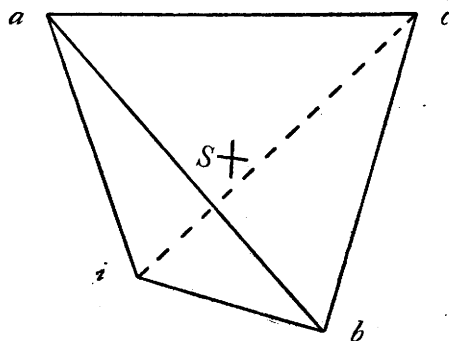


FIG. 2.

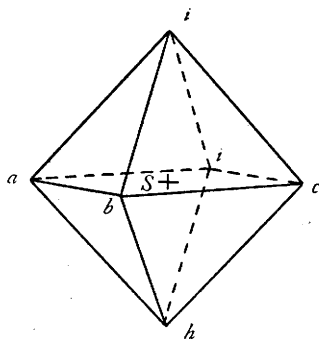
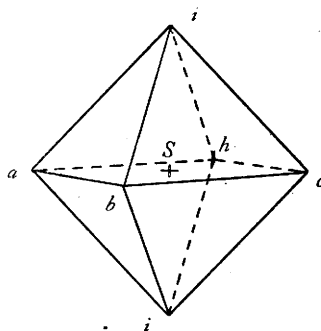


FIG. 3.



molecule as to give rise to a non-enantiomorphous product ; these are the two cases analogous to those illustrated in Figs. 2 and 3.

Although the intramolecular disturbance attending a change of valency might be expected to cause optical inversion, there is no reason to anticipate the existence of a non-enantiomorphous configuration at any moment during the formation of a septavalent nitrogen compound from an optically active substituted ammonium salt, if the transition from quinque- to septa-valency occurs by some orderly series of mechanical steps. We know, in fact, that the asymmetric

ammonium iodides preserve their optical activity during formation of the mercuriodides. The explanation thus offered seems rational and involves the principle enunciated by Pope and Harvey (*loc. cit.*), that during a change of valency the valency directions may change.

Since the evidence now brought forward inclines us not to regard the above mercuriodides as salts of the complex acid  $\text{HHgI}_3$  whilst we still consider the platinichlorides as salts of the acid  $\text{H}_2\text{PtCl}_6$ , it seemed desirable to attempt some experimental discrimination between the configurations represented in Figs. 2 and 3. If the acid  $\text{HHgI}_3$  is not a factor in determining the formation of the mercuriodides, the production of these salts would seem due to the use of a *mercuric* compound and the particular acidic groups associated with the metal would not be so likely to influence the formation of a sexavalent sulphur compound; it should therefore be possible to prepare salts corresponding to the mercuriodides and mercurichlorides in which the three halogen groups are replaced by three optically active acidic groups. Then, if the new salt have the configuration given in Fig. 2, or if it be merely a salt of the acid  $\text{HHgX}_3$  (X being the optically active group), fractional crystallisation should show it to be a mixture of the two substances (*d*-B, *d*-A,  $\text{Hg}2d\text{-A}$ ) and (*l*-B, *d*-A,  $\text{Hg}2d\text{-A}$ ), whilst if Fig. 3 represent the constitution and configuration of the new salt, the latter must be a single substance, potentially irresolvable, and its molecular rotatory power in aqueous solution should be of the order of thrice that of the optically active acid ion. The view taken above of the constitution of the mercuriodides is supported by the fact that we were able to prepare the following salt.

*Methylethylphenacylthetine Mercuri-d-bromocamphorsulphonate*,  
 $\text{S}(\text{CH}_3)(\text{C}_2\text{H}_5)(\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_5)(\text{C}_{10}\text{H}_{14}\text{OBr}\cdot\text{SO}_3\text{H})_2\text{Hg}\cdot\text{C}_{10}\text{H}_{14}\text{OBr}\cdot\text{SO}_3\text{H}.$

On adding a concentrated solution of mercuric oxide in *d*-bromocamphorsulphonic acid to an aqueous solution of *l*-methylethylphenacylthetine *d*-bromocamphorsulphonate, a white precipitate is produced which, after crystallisation from dilute alcohol, is obtained in minute, white scales decomposing at about  $180^\circ$ ; it is insoluble in ether or chloroform but sparingly soluble in water, acetone, or alcohol:

0.4512 gave 0.07855 HgS.  $\text{Hg} = 14.98.$

$\text{C}_{41}\text{H}_{57}\text{O}_{13}\text{Br}_3\text{S}_4\text{Hg}$  requires  $\text{Hg} = 15.23$  per cent.

After several recrystallisations, 0.3300 gram, made up to 25 c.c. with water, gave  $\alpha_D + 1^\circ 37'$  in a 2 dm. tube; whence  $[\alpha]_D + 60.9^\circ$  and  $[\text{M}]_D + 800^\circ$ . Within the limits of experimental error, this value is equal to  $+810^\circ$ , three times the molecular rotatory power of the

*d*-bromocamphorsulphonic ion. A preparation made from *d*-methyl-ethylphenacylthetine *d*-bromocamphorsulphonate, after careful purification, proved to be identical with the foregoing. 0.3512 gram, made up to 25 c.c. with water, gave  $\alpha_D + 1^\circ 43'$  in a 2 dm. tube, whence  $[\alpha]_D + 60.8^\circ$  and  $[M]_D + 798^\circ$ .

Although further investigation of this salt is needed and is now in progress, the facts that the preparations from the *d*- and *l*-thetine salts yield fractions having practically the same rotatory power, and that that rotatory power is very nearly thrice the molecular rotatory power of the optically active acid ion, indicate that the two sources yield the same and a single irresolvable product, and that the sexavalent sulphur atom is not a centre of optical activity because it contributes no appreciable amount to the molecular rotatory power of the mercuri-*d*-bromocamphorsulphonate.

The configuration of the thetine and selenetine mercuriodides and mercurichlorides would therefore seem to be that illustrated in Fig 3.

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