13. *The Synthetic Application of* o-β-*Bromoethylbenzyl Bromide. Part V. The Preparation and Properties of Thioisochroman, Selenoisochroman, Telluroisochroman, and of their Optically Active Derivatives.*

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The three *iso*chromans named above have been prepared by the interaction of o-β-bromoethylbenzyl bromide and sodium sulphide, selenide, and telluride, respectively. The heterocyclic ring in these compounds has considerable stability, and hence they possess many of the normal chemical properties of alkyl sulphides, selenides, and tellurides.

Each of these compounds has been combined with *p*-chlorophenacyl bromide to give the corresponding sulphonium, selenonium, and telluronium salts, in which the Group VI element has become 3-covalent and asymmetric; consequently each salt has been resolved *via* the bromocamphorsulphonates, and the optically active picrates isolated. 2-p-*Chlorophenacylthioisochromanium picrate*, $[M]_D$ $-242°$ and $+250°$, and the corresponding *seleno-picrate*, $[M]_D$ $-533°$ and $+504°$, have thus been obtained; they possess very high optical stability. 2-p-*Chlorophenacyltelluroisochromanium picrate* has not been isolated in optically pure condition, but the optically impure enantiomorphs have been isolated having $[M]_D$ $-632°$ and $+578°$: evidence is adduced that the optically pure picrate would have $[M]_D > 750°$. These telluronium salts are much less stable optically than the corresponding sulphonium and selenonium salts, and racemise moderately rapidly in boiling solvents; even so, however, the *l*-telluronium picrate in acetone solution at room temperature required *ca.* 20 days for complete racemisation. The markedly increasing rotation of the above salts, taken in the order of the sulphur, selenium, and tellurium members, is noteworthy.

The significance of these results is briefly discussed.

It has been shown by von Braun and Zobel (*Ber.*, 1923, **56**, 2142) that o-β-bromoethylbenzyl bromide reacts with sodium sulphide to furnish the liquid thio*iso*chroman (I), which they characterised as the crystalline methiodide. We find that the bromide reacts similarly with alcoholic sodium selenide and telluride, forming the crystalline analogues, *seleno*iso*chroman* and *telluro*iso*chroman*. The heterocyclic ring in each of these three compounds has considerable stability, and in this respect resembles the corresponding ring in the 2-substituted 1 : 2 : 3 : 4-tetrahydro*iso*arsinolines (Holliman and Mann, J., 1943, 547); consequently these compounds show the normal reactions of sulphides, selenides, and tellurides, respectively. Thus, the selenide and the telluride also combine readily with methyl iodide to give highly crystalline *methiodides*. The sulphide (I) combines with sodio-toluene-*p*-sulphonchloroamide (chloramine-T), furnishing *thioisochroman-p-toluenesulphonylimine* (II), whereas the selenide, similarly treated, ultimately furnishes *selenoisochroman oxide* (III) and toluene-*p*-sulphonamide, although these compounds may possibly unite in solution to form the unstable hydroxyselenonium toluene-*p*-sulphonamide. The selenide readily combines with chlorine and with bromine to give


(I.)   (II.)   (III.)
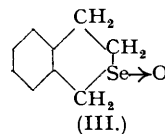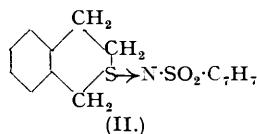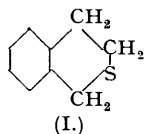
the crystalline *selenoisochroman dichloride* and *dibromide*, respectively; these are stable compounds which can be recrystallised unchanged from alcohol, but the dibromide, when treated with silver oxide or sodium hydroxide, is hydrolysed to the selenoxide (III). The telluride combines similarly with bromine to give the stable *telluroisochroman dibromide*. Although the selenoxide (III) is a crystalline compound, m. p. 104—105°, it slowly decomposes, even in a vacuum at room temperature, furnishing the parent selenide and other products; this type of decomposition is shown by many selenoxides (cf. Gaythwaite, Kenyon, and Phillips, J., 1928, 2287; Edwards, Gaythwaite, Kenyon, and Phillips, *ibid.*, p. 2293; Foster, *Rec. Trav. chim.*, 1935, **54**, 447).

Although dissymmetric selenoxides, of the type abSe→O, should, by analogy with the corresponding sulphoxides, be resolvable into optically active forms, no such resolution has yet been achieved (Gaythwaite,

Kenyon, and Phillips, *loc. cit.*). Our selenoxide (III) combines readily with *d*-bromocamphorsulphonic acid, forming the crystalline 2-*hydroxyseleno*isochromanium d-*bromocamphorsulphonate*, which is considerably more stable than the parent selenoxide; fractional recrystallisation of this salt from ethyl acetate did not, however, furnish any evidence of optical resolution.

The main interest in the new series of heterocyclic compounds of type (I) lies, however, in the chemical and optical properties of the salts which they form with alkyl halides and which contain the 3-covalent Group VI element. We have previously shown that salts formed by the addition of *p*-chlorophenacyl bromide have usually a greater stability than those formed with simple alkyl or phenacyl halides (Holliman and Mann, J., 1943, 550). Consequently, we have combined the three compounds of type (I) with *p*-chlorophenacyl bromide,
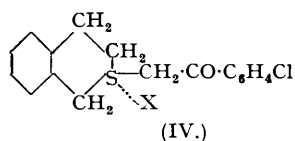
to furnish respectively the highly crystalline 2-p-*chlorophenacyl-thio-*, *-seleno-*, and *-telluro-*isochromanium *bromides* (cf. IV; X = Br). Each of these compounds contains an asymmetric 3-covalent Group VI element, and we have investigated their resolution and optical properties for two reasons. First, a eutropic series * of three optically active compounds had not previously been obtained, and a comparison of their optical properties was of obvious interest.

Secondly, their optical stability is dependent on at least two factors, and might well be low. Racemisation of a dissymmetric arsonium salt, *e.g.*, 2-phenyl-2-*p*-chlorophenacyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinolinium iodide (Holliman and Mann, *loc. cit.*), must depend solely on the formation of a "dissociation equilibrium," [abcdAs]I $\rightleftharpoons$ abcAs + dI; the arsonium ion itself, therefore, cannot racemise if it possesses high chemical stability. Our sulphonium salt (IV) and its analogues could, however, racemise either by the formation of a similar dissociation-equilibrium, of type [abcS]I $\rightleftharpoons$ abS + cI, or by the direct racemisation of the cation itself : if the ring system of (IV) is regarded as being in the plane of the paper, the *p*-chlorophenacyl group must be above or below this plane, and simple oscillation of this group between these positions would involve racemisation. Racemisation due to this cause has no counterpart in the quaternary ammonium and arsonium salts.

2-*p*-Chlorophenacylthio*iso*chromanium bromide (IV; X = Br) was therefore converted into the d-*bromo-camphorsulphonate* (IV; X = C$_{10}$H$_{14}$O$_4$BrS) which, after twelve recrystallisations from alcohol, was optically pure *l*-sulphonium *d*-sulphonate, having [M]$_D$ −13·1° in methyl alcohol; this compound possessed moderately high optical stability, since one hour's boiling in methyl-alcoholic solution reduced the activity only to [M]$_D$ −11·0°. This sulphonate was converted into the optically pure l-*thioisochromanium picrate* (IV; X = C$_6$H$_2$O$_7$N$_3$), having [M]$_D$ −242° in acetone solution. The activity of this picrate in acetone solution remained unchanged at room temperature for 24 hours; when the solution was heated under reflux, the activity fell to [M]$_D$ −232° after 1·25 hours and to [M]$_D$ −219° after 7·5 hours. The activity was unchanged when the picrate was rapidly recrystallised from boiling methyl or ethyl alcohol, but fell to [M]$_D$ −219° when a methyl-alcoholic solution was heated under reflux for one hour. The picrate therefore possesses a high degree of optical stability, but it should be noted that a "dissociation-equilibrium" (which would have involved the formation of *p*-chlorophenacyl picryl ether) could not occur in this compound, and loss of activity could have been caused therefore solely by direct racemisation of the cation.

The bromide (IV, X = Br) was similarly converted into the *l*-bromocamphorsulphonate, which on recrystallisation furnished the d-*sulphonium* l-*bromocamphorsulphonate*, and this in turn afforded the optically pure d-*thioisochromanium picrate*, having [M]$_D$ +250° in acetone solution.

The 2-*p*-chlorophenacylseleno*iso*chromanium bromide was similarly converted into the *d*-bromocamphor-sulphonate, which after only seven recrystallisations from alcohol furnished the optically pure l-*selenonium* d-*bromocamphorsulphonate* having [M]$_D$ −271° in ethyl alcohol and [M]$_D$ −293° in methyl alcohol; neither solution showed any change in rotation at room temperature for 24 hours, but heating under reflux of a methyl-alcoholic solution for 1 hour caused a reduction in rotation to [M]$_D$ −213°. The *d*-bromocamphorsulphonate in turn gave the optically pure l-*selenonium picrate*, having [M]$_D$ −533° in acetone solution. This picrate showed remarkable optical stability : its solution, in dry or in aqueous acetone, showed no change in rotation at room temperature for 2 days. Its rotation, in dry acetone solution, fell only to [M]$_D$ −518° after 30 minutes' and to [M]$_D$ −465° after 7·5 hours' heating under reflux; in aqueous acetone, it fell to [M]$_D$ −479° after 1 hour's refluxing. The rotation was unaffected by recrystallisation from methyl alcohol.

The *d*-bromocamphorsulphonate, when similarly treated with potassium mercuri-iodide, afforded the crystalline l-*selenonium mercuritri-iodide* (as IV; X = HgI$_3$);† this salt was slightly less optically stable than

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* The term "eutropic series of compounds" we define as a series of compounds consecutive members of which differ only in that they contain consecutive elements of any one sub-group of the Periodic Classification; for example, PCl$_3$, AsCl$_3$, SbCl$_3$, BiCl$_3$. There is an obvious need for a term to describe such a series. Tutton ("Crystalline Form and Chemical Constitution," 1926, 127) first used the term, without clear definition, apparently to denote a series of compounds such as we have defined that were in addition isomorphous; Drew and Landquist (J., 1935, 1480) later used the term "eutropic series" to denote consecutive elements in one sub-group of the Periodic Classification.

† The molecular rotation of this salt has been calculated throughout on the basis that it has the general formula [a$_3$Se][HgI$_3$], this being commonly assumed for similar sulphonium and selenonium salts (cf. Balfe, Kenyon, and Phillips, J., 1930, 2554; Cavell and Sugden, *ibid.*, p. 2572). The work of Evans, Mann, Peiser, and Purdie (J., 1940, 1209) indicates, however, that the anion must have the bivalent structure $\left[\begin{smallmatrix} I \\ I \end{smallmatrix} Hg \begin{smallmatrix} I \\ I \end{smallmatrix} Hg \begin{smallmatrix} I \\ I \end{smallmatrix} \right]^{--}$, and the usual formula of these salts should therefore be doubled.

the picrate, since the rotation of an acetone solution, having initially $[M]_{5780}$ $-421°$, fell to $[M]_{5780}$ $-352°$ after 9 days at room temperature.

The seleno*iso*chromanium bromide was also converted into the *l*-bromocamphorsulphonate, which on recrystallisation furnished the optically pure d-*selenonium* l-*sulphonate*, having $[M]_D$ $+291°$ in methyl alcohol, and this salt in turn furnished the d-*selenonium picrate*, having $[M]_D$ $+504°$ in acetone solution.

The only other known optically active selenium compound is phenylmethylselenetine platinichloride, which Pope and Neville (J., 1902, **81**, 1552) isolated in d- and l-forms, having $[M]_D$ $+55·0°$ and $-54·3°$, respectively, in acetone solution.

2-*p*-Chlorophenacytelluro*iso*chromanium bromide is markedly less stable chemically than its sulphur and selenium analogues, and when boiled with aqueous alcohol slowly gives the *telluroiso*chroman *hydroxybromide* and *p*-chloroacetophenone. The bromide in methyl-alcoholic solution was converted into the d-*bromocamphorsulphonate*, which was isolated by complete evaporation of the solution at room temperature; the residue, when first extracted with cold alcohol and then recrystallised from hot alcohol, furnished the optically impure l-*telluronium* d-*bromocamphorsulphonate*, the optically purest sample thus isolated having $[M]_D$ $-99°$ in methyl-alcoholic solution. The cold alcoholic extract, when again evaporated to dryness and extracted with petrol, furnished a residue of the optically impure d-telluronium d-bromocamphorsulphonate; in this case, the optically purest sample isolated had $[M]$ $+579°$ in methyl-alcoholic solution. These d-bromocamphorsulphonates in cold methyl- and ethyl-alcoholic solution exhibited slow mutarotation, which became rapid when the solutions were boiled. Consequently, although the solubilities of the two diastereoisomerides in cold ethyl alcohol were markedly different, even rapid recrystallisation of the l-telluronium d-sulphonate from alcohol gave only small progress towards the isolation of the optically pure salt; when it became clear that this isolation would involve excessive material and labour it was abandoned.

The mutarotation of this bromocamphorsulphonate in cold solvents presents some interesting features. Lowry and Gilbert (J., 1929, 2867) have shown that the mutarotation of l-phenyl-*p*-tolylmethyltelluronium d-bromocamphorsulphonate in cold acetone and ethyl acetate did not even approximate to a unimolecular reaction, a fact for which they were unable to suggest an explanation. (Their demonstration that the racemisation of the corresponding iodide was also not unimolecular may, however, have been vitiated by the speed of the racemisation and the experimental difficulties under which it was observed.) We find that the mutarotation of our l-telluronium d-bromocamphorsulphonate is also not unimolecular : this is clearly shown by the following values for the reaction coefficient (calculated as that of a unimolecular reaction, and expressed as hours^{-1} $\log_{10}$) of a 0·987% methyl-alcoholic solution of the chemically pure but optically impure salt thermostatically controlled at 22°, the first reading ($t = 0$) being made 18 minutes after the initial dissolution of the salt :

t (hrs.).	α_D.	$[M]_D$.	$k \times 10^4$.	t (hrs.).	α_D.	$[M]_D$.	$k \times 10^4$.	t (hrs.).	α_D.	$[M]_D$.	$k \times 10^4$.
0·00	$-0·18°$	$-32·2°$	—	3·25	$+0·54°$	$+97·0°$	663	13·75	$+1·34°$	$+241°$	552
0·25	$-0·08$	$-14·4$	972	4·25	$+0·66$	$+119$	623	16·75	$+1·42$	$+255$	528
0·50	0·00	0·00	894	5·50	$+0·81$	$+146$	610	20·75	$+1·51$	$+271$	525
0·75	$+0·06$	$+10·8$	808	6·75	$+0·94$	$+169$	604	24·75	$+1·59$	$+286$	573
1·25	$+0·19$	$+34·1$	780	8·25	$+1·07$	$+192$	599	28·75	$+1·61$	$+289$	545
1·75	$+0·30$	$+53·9$	750	9·75	$+1·15$	$+207$	572	35·75	$+1·65$	$+296$	515
2·50	$+0·41$	$+73·7$	671	11·75	$+1·26$	$+226$	564	48·75	$+1·66$	$+298$	—
								71·50	$+1·66$	$+298$	—

We have obtained similar results for other samples both of the l-telluronium and of the more soluble d-telluronium d-bromocamphorsulphonate. If the change which is occurring in our compound (and in Lowry and Gilbert's) is solely optical, *i.e.*, is unaccompanied by any chemical change, this departure from the unimolecular reaction is extremely difficult to interpret. After the mutarotation of our salt was complete, the solution was evaporated to dryness at room temperature, and (even after prolonged drying) the residue was no longer analytically quite pure. It is possible, therefore, that the course of the mutarotation was affected by interaction of the cation with the solvent or with impurities therein (*e.g.*, traces of water). We hope to examine this point in greater detail later, as the large but slow change in rotation of our salt, and of the corresponding picrate described below, makes them particularly suitable for mutarotation studies, and a fundamental point in the stereochemistry of tellurium may be involved. There is little doubt that the heterocyclic system in our cation is chemically unchanged during the mutarotation; on the other hand, the *p*-chlorophenacyl group can react with water and might conceivably react also with alcohols or ketones, and consequently mutarotation studies in solvents other than these are clearly required.

By treating the l-telluronium d-sulphonate with sodium picrate in methyl alcohol, the l-2-p-*chlorophenacyltelluroiso*chromanium *picrate* was readily precipitated; its rotation depended on the optical purity of the parent sulphonate and on the subsequent treatment of the picrate, but the optically purest sample we have isolated had $[M]_D$ $-632°$ in acetone solution. By estimating the proportion of inactive material in such a sample, the rotation of the remainder can be calculated as $[M]_D$ *ca.* $-750°$ (see p. 44), and there is reason to believe that the rotation of the optically pure picrate is even higher.

The d-telluronium d-sulphonate, which was never isolated in as optically pure a condition as its less soluble diastereoisomeride, furnished the d-picrate, the highest rotation of which we found to be $[M]_D$ $+575°$.

The l-telluronium picrate underwent very slow racemisation in acetone solution at room temperature, the

complete process requiring *ca.* 20 days. The reaction constant of this racemisation was determined with several samples of the picrate, and showed that this process also was not a unimolecular reaction. In this case again, however, analysis of the recovered picrate showed that it was no longer quite pure : it is significant that the speed of racemisation was increased markedly by the presence of a small proportion of water in the acetone, and the course of the above racemisation may well have been influenced by some·concurrent slight chemical reaction.

The magnitude of the rotation, and the comparative optical stability of our telluronium picrate are in striking contrast to those of Lowry and Gilbert's telluronium iodide (*loc. cit.*), the only other telluronium salt of type [abcTe]X to be obtained optically active; the maximum rotation recorded for their iodide in ethyl acetate was $[M]_{5461}$ —67° and +34°, and the longest period required for complete racemisation was *ca.* 30 minutes. Their salt, being a methyltelluronium iodide, would however undoubtedly be particularly liable to partial dissociation in solution, and its racemisation, unlike that of our telluronium picrate, might have been due both to this dissociation and to direct racemisation of the telluronium cation.

The considerable difficulties attending the isolation of our telluronium salt in an optically pure condition have prevented an accurate comparison of the optical properties of the three eutropic sulphonium, selenonium, and telluronium salts, although the considerable increase in the rotation of these salts, taken in this order, is unmistakable, and represents a factor in a eutropic series that has not previously been demonstrated. Even if the optically pure telluronium salt had been isolated, however, this comparison of the optical properties would have been very limited in scope, because the comparatively low solubilities of our bromocamphor-sulphonates restricted their conversion, by double decomposition in solution, into the even less soluble picrates and mercuritri-iodides, *i.e.*, into coloured salts the measurement of whose rotatory dispersion must necessarily have been limited to a very short range of wave-length. For our original purpose, salts that were both colourless and optically stable were clearly required. Furthermore, it would have been of great interest if the bromides or iodides of our optically active sulphonium, selenonium, and telluronium cations could have been isolated for comparison of their optical stabilities in solution, since these salts, unlike our picrates, might undergo racemisation by dissociation in solution and/or direct racemisation of their optically active cations.

<center>EXPERIMENTAL.</center>

All rotations were measured in a 4-dm. tube. Unless otherwise stated, the rotations were measured at 16° ± 1°, with the sodium-D line, λ = 5893, as the source of light. The reaction coefficient *k* has in all cases been calculated as that of a unimolecular reaction, and expressed in hours⁻¹ log₁₀.

Thioisochroman (I).—This was prepared by the following modification of von Braun and Zobel's method (*loc. cit.*). Sodium sulphide nonahydrate (36 g., 1·7 mols.) was added to a solution of *o*-β-bromoethylbenzyl bromide (25 g., 1 mol.) in alcohol (250 c.c.), and the mixture heated under reflux on a water-bath for 2 hours, the alcohol then being distilled off. The cold semi-solid residue was treated with water and twice extracted with ether. The combined extracts were washed with water, dried (calcium chloride), and distilled, the thioisochroman being isolated as a colourless liquid, b. p. 128—130°/15 mm., having a characteristic odour; 7·6 g., 56%. It readily formed the methiodide, m. p. 124° (efferv.) (Found : C, 41·0; H, 4·3. Calc. for $C_{10}H_{13}IS$: C, 41·1; H, 4·45%); von Braun and Zobel give m. p. 123°.

Thioisochromantoluene-p-sulphonylimine (II).—This readily crystallised when (I) was shaken with an excess of a cold aqueous solution of chloramine-T : colourless crystals from alcohol, m. p. 165° (Found : C, 60·4; H, 5·5; N, 4·5. $C_{16}H_{17}O_2NS_2$ requires C, 60·2; H, 5·3; N, 4·4%).

dl-2-p-*Chlorophenacylthioisochromanium Bromide* (IV, X = Br).—A mixture of equimolecular quantities of (I) and of *p*-chlorophenacyl bromide was continuously stirred whilst it was gently heated; as the temperature reached *ca.* 100°, the clear liquid rapidly crystallised. The cold product, recrystallised from water (charcoal), furnished the *monohydrate* of the bromide, m. p. 130° (Found : C, 50·8; H, 4·4; Cl, 8·8; Br, 19·9. $C_{17}H_{16}OClBrS,H_2O$ requires C, 50·8; H, 4·5; Cl, 8·8; Br, 19·9%). A hot alcoholic solution of the bromide, treated with an excess of aqueous sodium picrate, gave on cooling the corresponding dl-*picrate* (IV, X = $C_6H_2O_7N_3$), yellow crystals from alcohol, m. p. 175—175·5° (Found : C, 52·3; H, 3·5; N, 8·5. $C_{23}H_{18}O_8N_3ClS$ requires C, 51·9; H, 3·4; N, 7·9%).

Resolution of the 2-p-*Chlorophenacylthioisochromanium Ion.*—Solutions of the above bromide (46·5 g.) and of silver *d*-bromocamphorsulphonate (56·0 g., 1 mol.), each in a hot mixture of alcohol (300 c.c.) and water (60 c.c.), were mixed, boiled, filtered, and the alcohol then cautiously removed under reduced pressure. The cold residue consisted of a heavy oil and some water; the latter was decanted, and the oil, when triturated with alcohol (50 c.c.), readily furnished the crude crystalline sulphonium *d*-bromocamphorsulphonate, which was collected, washed with alcohol (50 c.c.) and ether, and dried; 36 g. Twelve recrystallisations from alcohol gave the optically pure l-*sulphonium d-bromocamphorsulphonate* (IV, X = $C_{10}H_{14}O_4BrS$), m. p. 168—170° (Found : C, 52·5; H, 5·1; S, 10·3. $C_{27}H_{30}O_5ClBrS_2$ requires C, 52·8; H, 4·9; S, 10·4%), α —0·10°, $[M]$ —13·1° (*c*, 1·172% in methyl alcohol). This rotation was not detectably changed by two more crystallisations from alcohol. Although the above resolution was performed in ethyl alcohol, rotations were determined in methyl alcohol because of the greater solubility of the salt in this solvent. A solution of the salt (0·2916 g.) in methyl alcohol (10 c.c.) was refluxed for 1 hour, cooled, and made up to 30 c.c. (*i.e.*, 0·972%); it then had α —0·07°, $[M]$ —11·0°, a very small degree of mutarotation having therefore occurred.

l-2-p-*Chlorophenacylthioisochromanium Picrate.*—Methyl-alcoholic solutions of the above sulphonate (14 times recrystallised) and of sodium picrate were cooled to 0° and mixed; the l-*picrate*, which was rapidly precipitated, was collected, washed in turn with methyl alcohol, water and methyl alcohol, and dried (Found : C, 52·4; H, 3·6; N, 8·3. $C_{23}H_{18}O_8N_3ClS$ requires C, 51·9; H, 3·4; N, 7·9%); m. p. 170—171°, α —0·60°, $[M]$ —242° (*c*, 0·330% in acetone). To check the completeness of the above resolution, the mother-liquor from the fourteenth recrystallisation of the sulphonate was similarly treated with sodium picrate; the l-picrate thus obtained had α —1·26°, $[M]$ —243° (*c*, 0·687% in acetone).

The rotation of this picrate remained unchanged when the salt was recrystallised from methyl or ethyl alcohol, and when its acetone solution was set aside at room temperature for 24 hours at 16°. In the following experiments, the picrate used in (*a*) and (*b*) had initially $[M]$ —243°; that in (*c*), $[M]$ —233°. (*a*) A solution of the picrate (0·1776 g.) in acetone (10 c.c.) was refluxed for 1·25 hours, cooled, and made up to 30 c.c. The solution (0·592%) then had α —1·04°, $[M]$ —232°. (*b*) Experiment (*a*) was repeated, with 7·5 hours' heating of the picrate (0·2076 g.). The final solution (0·692%) had α —1·14°, $[M]$ —219°, racemisation having proceeded to *ca.* 5%. (*c*) A 0·8% methyl-alcoholic solution of the picrate

was refluxed for 1 hour, and the solvent then removed in a desiccator at room temperature. A 0·660% acetone solution of the residual picrate had α −1·09°, [M] −219°.

The d-*thioisochromanium l-bromocamphorsulphonate* was similarly prepared from the *dl*-bromide and silver *l*-bromocamphorsulphonate. After twelve recrystallisations from ethyl alcohol, a 1·189% methyl-alcoholic solution had α +0·12°, [M] +15·5°, and after fourteen such recrystallisations, a 1·180% methyl-alcoholic solution had α +0·12°, [M] +15·6°; the final crop (Found : C, 52·55; H, 5·3%) had m. p. 168—170°, depressed to 135—144° by admixture with the *l*-sulphonium d-bromocamphorsulphonate.

d-2-p-*Chlorophenacylthioisochromanium picrate* was prepared from the *l*-sulphonate by the method previously described; yellow crystals (Found : C, 51·8; H, 3·4; N, 7·8%), m. p. 168—169° with preliminary softening; α +1·26°, [M] +250° (c, 0·671% in acetone).

Selenoisochroman.—The following method is an adaptation of that used by Morgan and Burstall (J., 1929, 1096) for seleno*cyclo*butane. Sodium (7 g.) was slowly added to alcohol (250 c.c.) contained in a 3-necked flask carrying a reflux water-condenser and two delivery tubes, only one of which reached to the bottom of the flask. When dissolution of the metal was complete, the mixture was cooled and diluted with water (6 c.c.). Hydrogen selenide, prepared by the action of dilute sulphuric acid on aluminium selenide (20 g.), was then bubbled through the solution whilst a vigorous current of hydrogen was passed through the shorter tube over the solution to prevent oxidation of the sodium selenide, which separated as a white powder. o-β-Bromoethylbenzyl bromide (25 g.) was then added, and the mixture refluxed for 3 hours, the rapid stream of hydrogen being maintained meanwhile. The alcohol was then distilled off, and the residue treated with water, and finally thoroughly extracted with ether. The extract was washed with water, dried (calcium chloride), and distilled, the *selenoisochroman* being obtained as a very pale yellow liquid, b. p. 150°/18 mm. (10·2 g., 58%), which rapidly crystallised; colourless crystals from methyl alcohol, m. p. 46—47° (Found : C, 54·5; H, 5·3. $C_9H_{10}Se$ requires C, 54·8; H, 5·1%). The aluminium selenide was prepared by igniting, by means of magnesium ribbon, an intimate mixture of finely powdered aluminium (2·7 g.) and selenium (12 g.).

2-*Methylselenoisochromanium Iodide.*—An excess of methyl iodide was added to a methyl-alcoholic solution of the selenide, which was then refluxed until the *iodide* started to crystallise. The mixture was cooled, diluted with ether, and the iodide collected and recrystallised from methyl alcohol; colourless needles, m. p. 146° (efferv.) (Found : C, 35·4; H, 4·1. $C_{10}H_{13}ISe$ requires C, 35·4; H, 3·8%).

Selenoisochroman Dichloride.—When solutions of the selenide and of chlorine (in excess), each in cold carbon tetrachloride, were mixed, the *dichloride* was rapidly precipitated; when collected and recrystallised from alcohol, it formed colourless plates, m. p. 138° (decomp. to green liquid) (Found : C, 39·9; H, 3·9. $C_9H_{10}Cl_2Se$ requires C, 40·3; H, 3·7%).

The *dibromide*, similarly prepared by using a solution of bromine (1 mol.), recrystallised from alcohol as pale yellow needles, m. p. 149° (decomp. with preliminary darkening) (Found : Br, 44·4. $C_9H_{10}Br_2Se$ requires Br, 44·8%).

Selenoisochroman Oxide (III).—(*a*) A mixture of the powdered dibromide and an aqueous N-sodium hydroxide solution (2 equivs.) was shaken until clear, and then evaporated to dryness in a desiccator at room temperature. The residue was extracted with chloroform, and the filtered extract, similarly evaporated, deposited colourless crystals of the *oxide*, m. p. 104—105° (Found : C, 49·4; H, 5·09. $C_9H_{10}OSe$ requires C, 50·7; H, 4·7%). When this preparation was repeated on a larger scale, considerable decomposition occurred owing to the longer time required for the two evaporations, and the residue formed a viscous, semi-solid mass, from which the pure selenide was ultimately isolated.

(*b*) Silver oxide (1·7 g., 1·54 mols.) was added to a solution of the dibromide (1·7 g.) in hot water (40 c.c.), and the mixture then boiled for 10 minutes (charcoal); the filtrate, cooled and evaporated in a desiccator at room temperature, gave a crystalline residue of the crude oxide, which after recrystallisation from dioxan had m. p. 100—102° (Found : C, 50·0; H, 4·9%). The odour of the selenide was detected during the above boiling; evaporation of the aqueous filtrate at 30—40° gave much decomposition, and the residue remained liquid.

The selenoxide is freely soluble in water, methyl and ethyl alcohol, and in chloroform, less so in acetone, and almost insoluble in benzene and carbon tetrachloride. An aqueous solution, treated with concentrated hydrochloric acid, furnished the dichloride, m. p. 140° (efferv., mixed and unmixed). An alcoholic solution of the oxide, treated with alcoholic picric acid, gave a yellow precipitate which, after one and two recrystallisations from alcohol, had m. p. 97—103° and 120—123°, respectively; the latter value being unchanged by further crystallisation; analysis indicated that the final compound was the 2-*ethoxyselenoisochromanium picrate* (A) instead of the expected hydroxy-picrate (B) [Found : C, 43·8; H, 3·7; N, 9·1. $C_{17}H_{17}O_8N_3Se$ (A) requires C, 43·4; H, 3·6; N, 8·9%. $C_{15}H_{13}O_8N_3Se$ (B) requires C, 40·7; H, 2·9; N, 9·5%].

*Action of Chloramine-*T.—A solution of the selenide (0·749 g.) and anhydrous chloramine-T (0·862 g., 1 mol.) in alcohol (20 c.c.) was refluxed for 20 minutes, filtered to remove sodium chloride, and evaporated in a desiccator at room temperature. The semi-solid residue, when triturated with ether, furnished a white solid, which, after two recrystallisations from acetone, had m. p. 119° (efferv.) and was nitrogen-free; this compound was a particularly pure sample of the selenoxide, since its aqueous solution, treated with concentrated hydrochloric acid, deposited the dichloride, white crystals from alcohol, m. p. 140° (efferv., mixed and unmixed). The original ethereal washings furnished the selenide (identified as the methiodide), whereas the acetone mother-liquors afforded toluene-*p*-sulphonamide, white crystals from benzene, m. p. 133—135° (mixed and unmixed).

2-*Hydroxyselenoisochromanium* d-*Bromocamphorsulphonate.*—A solution of the selenoxide (III) in dilute hydrochloric acid (1 mol. of acid) was mixed with an aqueous solution of silver d-bromocamphorsulphonate (1 mol.), boiled for 5 minutes, filtered, and cooled. Colourless crystals of the *hydroxy*-d-*bromocamphorsulphonate*, m. p. 125—133° (decomp.), were deposited; α +1·20°, [M] +292° (c, 0·539% in alcohol), the rotation being observed 20 minutes after contact of the solute and solvent; α +1·09°, [M] +260° (c, 0·549% in chloroform). This salt was now recrystallised four times from ethyl acetate, from which it separated in hard crystals which apparently contained solvent of crystallisation, for they effloresced in a vacuum at room temperature; m. p. 117—123° (decomp.) (Found : C, 43·3; H, 5·1. $C_{19}H_{25}O_5BrSSe$ requires C, 43·5; H, 4·8%); α +1·12°, [M] +266° (c, 0·551% in chloroform).

The ethyl acetate mother-liquors, when set aside for several days, deposited fine needles which were entirely different in appearance from those above, and did not effloresce in a vacuum; m. p. 114—118° (Found : C, 42·6; H, 5·2%). A 0·563% chloroform solution had, however, α +1·13°, [M] +263°.

The pure bromocamphorsulphonate slowly decomposed to a brown liquid when kept at room temperature even in the dark; this decomposition was much slower than that of the selenoxide.

dl-2-p-*Chlorophenacylselenoisochromanium Bromide.*—*p*-Chlorophenacyl bromide (8·2 g.) was added to a solution of the selenide (7·3 g., 1 mol.) in hot alcohol (50 c.c.), and the solution refluxed for 5 minutes and then cooled. After the semi-solid product had been diluted with benzene (ca. 20 c.c.), the *bromide* was collected, washed with alcohol and benzene, and recrystallised from alcohol; colourless crystals (12·2 g.), m. p. 122° (Found : C, 47·8; H, 3·55. $C_{17}H_{16}OClBrSe$ requires C, 47·4; H, 3·7%). The dl-*picrate* was readily obtained when alcoholic picric acid was added to a boiling alcoholic solution of the bromide; yellow crystals from alcoholic acetone, m. p. 167—168° (Found : N, 7·4. $C_{23}H_{18}O_8N_3ClSe$ requires N, 7·3%).

Resolution of the 2-p-*Chlorophenacylselenoisochromanium Ion.*—Solutions of the above bromide (12·7 g.) and of silver

d-bromocamphorsulphonate (14·2 g., 1 mol.), each in hot 90% alcohol (200 c.c.), were mixed, boiled for a short period, and filtered. The filtrate, when set aside, deposited the optically impure crystalline *selenoisochromanium* d-*bromocamphor-sulphonate*, m. p. 155—157°. This was recrystallised seven times from alcohol, the consecutive crops having these rotations in alcoholic solution :

G. solute/100 c.c. solvent	0·613	0·720	0·447	0·363	0·390	0·343	0·341
α	−0·45°	−0·88°	−0·64°	−0·56°	−0·65°	−0·57°	−0·56°
[M]	− 120	− 202	− 236	− 254	− 275	− 275	− 271

The final crop was therefore the optically pure *l*-selenonium *d*-sulphonate; m. p. 157—159° with preliminary softening (Found : C, 48·8; H, 4·6. $C_{27}H_{30}O_5ClBrSSe$ requires C, 49·1; H, 4·5%). This salt is considerably more soluble in methyl alcohol, in which a 0·681% solution had α −1·21°, [M] −293°. No change in rotation of solutions in either solvent at room temperature could be detected over 24 hours. A 1·976% solution in methyl alcohol was refluxed for 1 hour and cooled; the solution, diluted to 0·659%, had α −0·85°, [M] −213°. The rotations of the ions being assumed to be additive, this indicates that the racemisation of the selenonium ion had progressed by *ca.* 14%.

1-2-p-*Chlorophenacylselenoisochromanium Picrate.*—A saturated methyl-alcoholic picric acid solution (10 c.c.) was added with stirring to a solution of the above optically pure *l*-selenonium *d*-sulphonate (0·8 g.) in methyl alcohol (30 c.c.) previously cooled to 0°. The precipitated l-*selenonium picrate* was collected, washed with alcohol and water, and dried, a further crop being obtained by cautious dilution of the original filtrate with water; the united crops (0·6 g.) had m. p. 174—175° (Found : C, 47·4; H, 3·4; N, 7·6. $C_{23}H_{18}O_8N_3ClSe$ requires C, 47·7; H, 3·1; N, 7·3%); α −0·80°, [M] −531° (c, 0·218% in acetone). The preparation was repeated but with sodium picrate; the united crops had α −1·55°, [M], −533° (c, 0·421% in acetone).

A portion of this *l*-picrate was recrystallised from methyl alcohol; its m. p. was unchanged, and a 0·396% acetone solution had α −1·43°, [M] −522°. A 0·409% solution of the *l*-picrate, in acetone containing 2% of water, had α −1·41°, [M] −499°. None of the above solutions showed any change in rotation at room temperature during 48 hours; although the presence of water in the acetone causes a fall in rotation, this is evidently at room temperature a solvent effect and is not due to partial racemisation.

In the following experiments to determine the degree of optical stability of the *l*-picrate in dry and in aqueous acetone, and in methyl alcohol, the picrate used in (*a*) and (*b*) had initially [M] −531°, that in (*c*) [M] −499°, and that in (*d*) [M] −522°. (*a*) A solution of the picrate (0·0988 g.) in acetone (10 c.c.) was heated under reflux for 30 minutes, cooled, and diluted to 30 c.c. (*i.e.*, 0·329%). It then had α −1·18°, [M] −518°, racemisation having therefore proceeded by *ca.* 2·4%. (*b*) Experiment (*a*) was repeated, but with 7·5 hours' refluxing and 0·1307 g. of picrate. The diluted solution (0·436%) had α −1·41°, [M] −465°, racemisation having proceeded by *ca.* 16%. (*c*) A solution of the picrate (0·1530 g.) in acetone (10 c.c.) and water (0·5 c.c.) was refluxed for 1 hour. After dilution with acetone as before, the solution (0·510%) had α −1·69°, [M] −479°; racemisation, *ca.* 4%. (*d*) A 1·00% solution in methyl alcohol was refluxed for 1 hour, cooled, and evaporated to dryness in a desiccator at room temperature; a 0·357% acetone solution of the residue had α −1·21°, [M] −491°; racemisation, *ca.* 5%.

In a preliminary note (*Nature*, 1943, **152**, 750) it was stated that refluxing of an acetone solution of this picrate for 1·25 hours caused complete racemisation; this statement is misleading, as it was subsequently found that this rapid racemisation was due to an unsuspectedly high proportion of water in the particular acetone used.

The inactive bromide was now treated as before but with silver *l*-bromocamphorsulphonate. Nine recrystallisations of the product from alcohol gave the optically pure d-*selenoisochromanium* l-*bromocamphorsulphonate*, unchanged by further recrystallisations; m. p. 158—160° (Found : C, 49·0; H, 4·8%); α +0·56°, [M] +276° (c, 0·332% in alcohol).

d-2-p-*Chlorophenacylselenoisochromanium Picrate.*—This was isolated precisely as the *l*-picrate. A 0·347% acetone solution of the dried but unrecrystallised salt had α +1·21°, [M] +504°; after recrystallisation from methyl alcohol, this d-*picrate* had m. p. 170—171·5° (Found : C, 47·85; H, 3·5; N, 7·3%), α +1·50°, [M] +504° (c, 0·430% in acetone). Several preparations of this picrate had rotations closely approaching this value. The difference between the values obtained for the rotations of the *l*- and the *d*-picrate is, however, difficult to explain.

The l-*Selenoisochromanium Mercuritri-iodide.*—Two solutions in methyl alcohol were prepared, one containing the *l*-selenonium *d*-bromocamphorsulphonate (1 mol.) and the other both potassium iodide (1 mol.) and mercuric iodide (1 mol.). These were cooled to 0° and rapidly mixed; the l-*mercuritri-iodide* separated as a pale yellow microcrystalline powder, m. p. 65—100° (decomp.) (Crop I), which was collected, washed with methyl alcohol, and dried. Cautious dilution of the original mother-liquor with water gave an emulsion, which ultimately deposited a yellow crystalline powder of unchanged m. p. (Crop II). A 0·273% acetone solution of Crop I at 16° gave the following rotations after the stated period from initial preparation of the solution :

Time (hrs.).	α_{5780}	$[M]_{5780}$	α_{5461}	$[M]_{5461}$	$\alpha_{5780}/\alpha_{5461}$
1·5	−0·56°	−478°	−0·65°	−554°	0·863
18·5	−0·55	−469	−0·61	−520	0·902
65	−0·49	−418	−0·54	−460	0·909

A 0·292% acetone solution of Crop II at 16° had α_{5780} −0·67°, $[M]_{5780}$ −535°, α_{5461} −0·74°, $[M]_{5461}$ −591°; $\alpha_{5780}/\alpha_{5461}$ 0·905.

To investigate this mutarotation more fully, this preparation was repeated on a larger scale; analysis showed that only Crop II was the chemically pure mercuritri-iodide (Found : Crop I, C, 23·25; H, 2·2. Crop II, C, 21·6; H, 2·0. $C_{17}H_{16}OClI_3HgSe$ requires C, 21·9; H, 1·7%), although the cations in the two crops were undoubtedly chemically identical. The mutarotation of Crop II was slower than that of Crop I, but was not appreciably affected by the concentration; the initial rotations of both crops were smaller than those obtained in the earlier experiment, owing to the longer time required to isolate the larger crops.

The following table shows the rotations after specified times of (A) a 0·674% solution of Crop I; (B) a 0·671% solution of Crop II; (C) a 0·271% solution of Crop II, all in acetone at 18°.

	Time.	α_{5893}	$[M]_{5893}$	α_{5780}	$[M]_{5780}$	α_{5461}	$[M]_{5461}$
(A)	35—60 Mins	−0·86°	−297°	−0·91°	−315°	−1·07°	−370°
	1 Day	−0·79	−273	−0·87	−301	−1·01	−349
	9 Days	−0·33	−114	−0·40	−138	−0·46	−159
(B)	35—60 Mins.	−1·04	−361	−1·17	−406	−1·37	−476
	9 Days	−0·99	−344	−1·07	−372	−1·28	−444
(C)	35—50 Mins.	−0·44	−378	−0·49	−421	−0·56	−481
	9 Days	−0·37	−318	−0·41	−352	−0·50	−430

Many attempts were made to convert the *l*-selenonium *d*-bromocamphorsulphonate into a salt having an inactive colourless cation (*i.e.*, without absorption in the visible spectrum), so that the rotatory dispersion and the absorption spectrum could be correlated. Difficulties due primarily to comparative solubilities nullified all such attempts.

Telluroisochroman.—An aqueous solution of sodium telluride was prepared (cf. Balfe, Chaplin, and Phillips, J., 1938, 344) by adding rongalite (34 g.) to a solution of sodium hydroxide (26 g.) in water (100 c.c.) contained in a flask fitted with a reflux water-condenser and an inlet tube, by which the air was replaced by a stream of coal-gas; finely divided tellurium (15 g., precipitated by sulphur dioxide reduction of a solution of the dioxide in hydrochloric acid) was added, and the mixture heated on a water-bath for 30 minutes with frequent shaking, a permanganate-coloured solution being thus obtained. Alcohol (100 c.c.) was now added, followed by a solution of o-β-bromoethylbenzyl bromide (25 g.) in hot alcohol (150 c.c.), and the mixture, which formed two layers, was then heated for a further 2 hours with occasional vigorous shaking. The alcohol was now distilled off, the stream of coal-gas having been maintained throughout the preparation until the distillation was complete.

The residue was cooled, broken up, and shaken vigorously with a mixture of water (300 c.c.) and ether (300 c.c.), the undissolved residue being then filtered off. The ethereal extract was separated, washed with water, dried (sodium sulphate), and distilled, the *telluroisochroman* being collected as a pale yellow liquid (8·5 g., 37%), b. p. 116—126°/0·3 mm., which readily crystallised on cooling. A second crop (3·8 g.) was obtained when the undissolved residue was extracted with hot alcohol (50 c.c.), and the extract filtered and cooled. The united crops were recrystallised from methyl alcohol, the solution being cooled in an atmosphere of carbon dioxide; silky needles, m. p. 63·5—64° (Found : C, 44·1; H, 4·1; *M*, ebullioscopic in 0·860% alcoholic solution, 244. $C_9H_{10}Te$ requires C, 43·9; H, 4·1%; *M*, 246).

2-Methyltelluroisochromanium Iodide.—The telluride rapidly dissolved when added to an excess of cold methyl iodide, and the yellow solution readily deposited the crystalline *iodide*, which, after addition of alcohol to complete the precipitation, was collected and recrystallised from 50% aqueous methyl alcohol, from which it separated as a *mono-methyl-alcoholate*, m. p. 260° (efferv.) in a sealed tube (Found : C, 31·7; H, 3·8. $C_{10}H_{13}ITe,CH_4O$ requires C, 31·4; H, 4·05%). The iodide is almost insoluble in boiling ethyl alcohol.

Telluroisochroman Dibromide.—When a solution of bromine (1 mol.) in carbon tetrachloride was added to one of the telluride in chloroform, rapid addition occurred, followed by separation of the *dibromide*, which, twice recrystallised from alcohol, furnished colourless crystals, m. p. 166—167° (Found : C, 26·8; H, 2·8. $C_9H_{10}Br_2Te$ requires C, 26·6; H, 2·5%).

Action of Hydrogen Peroxide on the Telluride.—Aqueous hydrogen peroxide ("20-vol.") was added dropwise to a boiling alcoholic solution of the telluride until no further precipitate was obtained. The white amorphous product was collected, thoroughly washed in turn with alcohol, water and alcohol again, and dried. It then darkened and shrunk when heated to 180° but did not melt below 270°; it was insoluble in all the usual organic solvents except chloroform, and could not be recrystallised. These properties are closely similar to those of the oxidation products of other tellurides described by Balfe, Chaplin, and Phillips (*loc. cit.*). The composition of the compound indicated that the oxidation had proceeded beyond the tellurone stage, without, however, complete conversion into the "hydroxy-perhydrate" stage, of type $a_2Te(OH)\cdot O\cdot OH$, described by these authors (Found : C, 37·8; H, 4·1. Calc. for $C_9H_{10}O_2Te$: C, 38·9; H, 3·6%. $C_9H_{12}O_3Te$ requires C, 36·6; H, 4·1%).

dl-2-p-Chlorophenacyltelluroisochromanium Bromide.—When *p*-chlorophenacyl bromide (1 mol.) was added to a solution of the telluride in boiling alcohol, the *bromide* was rapidly precipitated; after 5 minutes' boiling, it was collected from the hot solution, washed with alcohol, and recrystallised from methyl alcohol; m. p: 161—163° with preliminary softening (Found : C, 42·8; H, 3·6. $C_{17}H_{16}OClBrTe$ requires C, 42·5; H, 3·3%). The bromide is only slightly soluble in boiling ethyl alcohol, but moderately soluble in boiling methyl alcohol.

This preparation was successfully repeated on several occasions; on one occasion, however, the boiling alcoholic solution remained clear, but on cooling deposited *telluroisochroman hydroxybromide*, m. p. 145° after two recrystallisations from alcohol (Found : C, 31·1; H, 3·0. $C_9H_{11}OBrTe$ requires C, 31·3; H, 3·2%); its identity was confirmed by the addition of aqueous hydrobromic acid to its alcoholic solution, whereby on cooling long colourless needles of the dibromide were deposited, m. p. 166—167° alone and when mixed with an authentic sample (Found : C, 26·9; H, 2·3%). That this result was due to the presence of water in the alcohol was demonstrated by the following experiment. A mixture of the bromide (1 g.), alcohol (20 c.c.), and water (0·5 c.c.) was refluxed for 45 minutes. The solution, which had rapidly become clear, was then cooled and evaporated to dryness in a vacuum at room temperature. The glassy residue, when triturated with ether, readily gave a crystalline residue which was collected. The ethereal filtrate contained *p*-chloroacetophenone, detected by its odour and by conversion into the semicarbazone, m. p. 204—206° (Found : C, 52·2; H, 5·5; N, 19·8. Calc. for $C_9H_{10}ON_3Cl$: C, 51·1; H, 4·7; N, 19·9%). The crystalline residue had m. p. 80—120°, raised to 140—168° by recrystallisation from alcohol; it was evidently the impure telluride hydroxybromide, since treatment with hydrobromic acid (as above) furnished the crystalline dibromide, m. p. 165—165·5°, alone and mixed with an authentic sample (Found : C, 27·15; H, 2·7%).

dl-2-p-Chlorophenacyltelluroisochromanium Picrate.—This was immediately precipitated when hot methyl-alcoholic solutions of the bromide and of sodium picrate were mixed; yellow crystals, m. p. 198—199° (decomp.) after recrystallisation from acetone (Found : C, 44·5; H, 3·3; N, 6·6. $C_{23}H_{18}O_8N_3ClTe$ requires C, 44·0; H, 2·9; N, 6·7%); it is almost insoluble in hot methyl and ethyl alcohol, and only slightly soluble in hot acetone.

Partial Resolution of the 2-p-Chlorophenacyltelluroisochromanium Ion.—(A). The *l*-ion. (1) Solutions of the telluronium bromide (2 g.) and of silver *d*-bromocamphorsulphonate (2 g., 1 mol.), each in boiling methyl alcohol (100 c.c. and 50 c.c.), were mixed, boiled for 2 minutes, filtered, and the filtrate evaporated in a vacuum desiccator. The partly crystalline residue, which had an odour resembling that of an aryl alkyl ketone, was triturated with cold alcohol (10 c.c.), and the insoluble white crystalline salt collected, and washed with alcohol and ether; m. p. 143—154°; 1 g. Recrystallisation from ethyl alcohol furnished the chemically pure but optically impure l-*telluronium* d-*bromocamphorsulphonate*, colourless needles, m. p. 147—158° (Found : C, 45·7; H, 4·6. $C_{27}H_{30}O_5ClBrSTe$ requires C, 45·7; H, 4·3%), α —0·55°, [M] —99° (*c*, 0·987% in methyl alcohol). This solution showed the following mutarotation at 15° :

Time, hrs.	α.	[M].	Time, hrs.	α.	[M].	Time, hrs.	α.	[M].
2	−0·26°	− 47°	26	+0·67°	+120°	95	+1·44°	+259°
4	−0·12	− 21·5	29	+0·75	+135	120	+1·52	+273
6	−0·02	− 3	32	+0·805	+145	143	+1·575	+282
8	+0·10	+ 18	47	+1·05	+188	168	+1·61	+289
23	+0·62	+110	56	+1·155	+207	215	+1·65	+296

(2) The above preparation was repeated upon quadruple quantities. The less soluble fraction of the sulphonate, after being extracted with cold alcohol but not recrystallised, had $α^{16°}$ −0·45°, [M] −81° (*c*, 1·007% in methyl alcohol); these readings were taken 10 minutes after wetting the salt with the solvent, and after 18 hours had changed to $α^{16°}$ +0·48°, [M] +85°. Another portion of this salt (0·2170 g.) was refluxed with methyl alcohol (10 c.c.) for 1 hour : the solution was cooled, diluted to 30 c.c. (*i.e.*, 0·723% solution), and then had α +0·95°, [M] +233°.

(3) In another similar preparation, the extracted but unrecrystallised sulphonate had $a^{16°}$ $+0.15°$; $[M]$ $+38°$ (c, 0·705% in methyl alcohol) within 15 minutes of dissolution. A portion of this salt was recrystallised from benzene, and then had $a^{16°}$ $+0.11°$, $[M]$ $+28°$ (c, 0·702% in methyl alcohol). A second portion was rapidly recrystallised from ethyl alcohol, and was then chemically pure (Found : C, 45·8; H, 4·3%), m. p. 145—152°; the mutarotation of a 0·987% methyl-alcoholic solution of this recrystallised sample is given on p. 39.

(B). *The d-ion.* (1) The cold ethyl-alcoholic extract obtained in Experiment (A, 1) was evaporated in a vacuum desiccator, and the optically impure d-telluronium d-bromocamphorsulphonate obtained as a friable glass, $a^{15°}$ $+2.79°$, $[M]$ $+498°$ (c, 0·393% in methyl alcohol), and gave the following values during mutarotation :

Time (hours)	3	19	27	67	91	115	139	187	235
$a^{15°}$	$+2.72°$	$+2.49°$	$+2.38°$	$+2.02°$	$+1.91°$	$+1.86°$	$+1.80°$	$+1.79°$	$+1.75°$
$[M]^{15°}$	486	445	425	361	341	332	321	320	312

(2) In another similar preparation, the friable glass thus obtained was thoroughly triturated with petrol (b. p. 40—60°); the residual hygroscopic salt, m. p. 55—70°, had $a^{16°}$ $+1.74°$, $[M]$ $+579°$ 15 mins. after preparation and $a^{16°}$ $+1.59°$, $[M]$ $+529°$ 19 hrs. after (c, 0·533% in methyl alcohol).

The l-Telluronium Picrate.—When a methyl-alcoholic solution of picric acid was added to a solution of the l-telluronium d-bromocamphorsulphonate (2 g., having $[M]$ $-81°$ in methyl alcohol) in cold methyl alcohol (200 c.c.), the optically impure l-*picrate* was immediately precipitated. It was collected, washed with methyl alcohol, and dried (Found : C, 44·1; H, 3·0; N, 6·6. $C_{22}H_{18}O_8N_3ClTe$ requires C, 44·0; H, 2·9; N, 6·7%); m. p. 192—193° (decomp.), a $-0.37°$, $[M]$ $-280°$ (c, 0·207% in acetone). Cautious addition of water to the original mother-liquor precipitated a much more active sample of the picrate, $a^{14°}$ $-1.34°$, $[M]$ $-600°$ (c, 0·350% in acetone).

The fact that the latter sample was appreciably more soluble in acetone than the former enabled optical purification to be taken further. The former sample, $[M]$ $-280°$, was vigorously shaken with acetone (30 c.c./1 g. of picrate), and the mixture then filtered; the undissolved residue had $[M]$ $-77°$ (c, 0·183% in acetone). The filtrate, evaporated to dryness at room temperature, deposited the chemically pure picrate (Found : C, 44·5; H, 2·9%), m. p. 187° (decomp.), $a^{14°}$ $-1.38°$, $[M]$ $-632°$ (c, 0·342% in acetone).

A 0·418% solution of this picrate in acetone which contained 0·4% of water underwent very slow racemisation : since the solution was not thermostatically controlled, its temperature at each reading is given :

Days.	Temp.	a	$[M]$.	$k \times 10^4$.	Days.	Temp.	a.	$[M]$.	$k \times 10^4$.
—	13·5°	$-1.68°$	$-630°$	—	10	16°	$-0.35°$	$-131°$	28
1	13·5	-1.455	-546	26	12	17	-0.22	-82.5	30·5
3	13	-1.155	-433	23	14	17	-0.12	-45	34
5	14	-0.90	-340	23	17	16·5	-0.06	-22.5	35
7	14	-0.65	-240	25	19	16	-0.03	-11	38
8·5	15	-0.48	-180	28	21	16	0	0	—

After racemisation was complete, the solvent was removed in a vacuum at room temperature; the residue had a pronounced odour of an aromatic ketone, but when washed with ether it furnished the chemically pure picrate (Found : C, 43·7; H, 3·2; N, 7·0%).

Another solution of the above picrate (having $[M]$ $-632°$) in acetone containing *ca.* 2% of water showed much more rapid racemisation. For this purpose, the picrate (0·1142 g.) was dissolved in acetone, water (0·5 c.c.) added, and the solution made up to 30 c.c. with acetone, giving a 0·347% solution. This furnished the following readings :

Hours.	Temp.	a.	$[M]$.	$k \times 10^3$.	Hours.	Temp.	a.	$[M]$.	$k \times 10^3$.
—	14°	$-1.36°$	$-560°$	—	27	14°	$-0.44°$	$-180°$	18
2	14	-1.11	-457	44	42	14	-0.31	-130	15
3	14	-1.02	-420	42	66	15	-0.18	-74	13
4	14	-0.96	-395	38	90	15	-0.08	-33	14
6	14	-0.87	-360	31	114	16	-0.03	-12	14·5
18	14	-0.59	-240	20	139	16	0	0	—

Removal of the solvent as before again gave a residue having an odour of a ketone; recrystallisation from aqueous alcohol gave a product, m. p. 195° (decomp. with preliminary darkening), whose composition suggests a *monohydrate* of the picrate (Found : C, 42·8; H, 3·35. $C_{23}H_{18}O_8N_3ClTe,H_2O$ requires C, 42·8; H, 3·1%).

A higher value for the rotation of the picrate was obtained by the following experiment. A saturated acetone solution of the dl-picrate was found (by direct evaporation in a vacuum at room temperature) to contain 0·068 g. of picrate/30 c.c. This volume of an acetone solution, saturated with respect to both the l- and the dl-picrate, was found by similar treatment to contain 0·396 g. of the mixed product, which in 0·352% acetone solution had $a^{15.5°}$ $-1.40°$, $[M]$ $-624°$; subtraction of the above weight of the dl-picrate shows that the l-picrate had $[M]$ $-753°$. This estimation ignores the mutual influence of the picrates on their solubilities, and also the racemisation that must have occurred during the second slow evaporation. The optically pure picrate has undoubtedly an even higher rotation than that calculated.

The d-Telluronium Picrate.—The more soluble, optically impure, d-telluronium d-bromocamphorsulphonate, having $[M]$ $+579°$, was treated in methyl-alcoholic solution with sodium picrate (as already described) to precipitate the d-*picrate*, and a second crop obtained by dilution of the filtrate with water. A 0·178% acetone solution of the first crop had $a^{15.5°}$ $+0.42°$, $[M]$ $+370°$, and a 0·190% solution of the second crop had $a^{15.5°}$ $+0.19°$, $[M]$ $+206°$. These crops were united and extracted with cold acetone (30 c.c./g.); the undissolved material was filtered off, and the filtrate on evaporation gave the d-picrate, $a^{15.5°}$ $+1.28°$, $[M]$ $+578°$ (c, 0·347% in acetone). This was again extracted with insufficient cold acetone for complete dissolution, and the filtrate on evaporation gave a further sample of the d-picrate, which had $a^{15.5°}$ $+1.27°$, $[M]$ $+575°$ (c, 0·347% in acetone); this sample had m. p. 189° (decomp.) and was chemically pure (Found : C, 44·1; H, 3·3; N, 6·95%), but still optically impure.