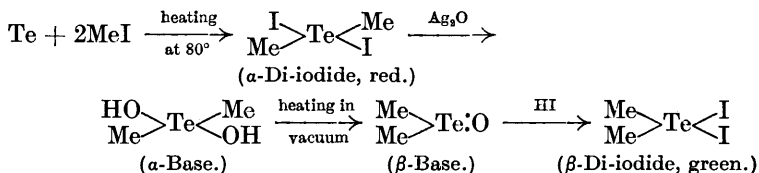


LXXXII.—*Non-existence of Isomerism among the Dialkyltelluronium Dihalides.*

By HARRY DUGALD KEITH DREW.

VERNON (J., 1920, **117**, 86, 897; 1921, **119**, 105, 687) obtained two forms of dimethyltelluronium di-iodide and thence two distinct bases. He formulated these substances as follows :



and postulated planar distribution of the valencies of the tellurium atom. He obtained similar results with the dichlorides and dibromides, and was thus led to assign these substances to two distinct series (the α- and the β-series) of isomeric compounds.

More recently, Lowry, Gilbert, and their collaborators have studied this supposed isomerism and have extended the theory to the diethyl homologues (J., 1928, 307, 1997, 3179; *J. Soc. Chem. Ind.*, 1928, **47**, 1246). They appear to attribute the isomerism to the non-equivalence, from the point of view of electron structure, of the halogen-tellurium linkings.

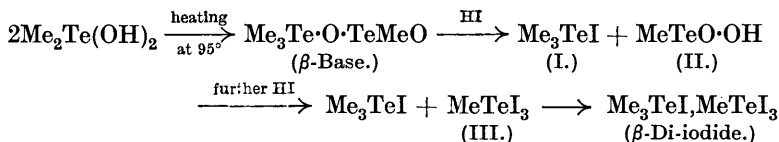
The present author, considering the preponderance of both theoretical and experimental evidence to be against the occurrence of isomerism of the kind postulated, has re-examined the dimethyltelluronium di-iodides and dibromides, and the two bases, and has reached the following conclusions.

The long-known compounds of the α-series are, as would be expected from their mode of preparation, of the normal type, in which tellurium has probably a tetrahedral valency distribution. They are broadly non-polar in character.

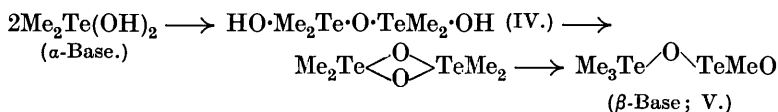
The compounds of the β-series are not isomeric with the corresponding members of the α-series, but are complex substances, of salt-like character, having the same empirical formulæ.

The β-base is a mixed anhydride, of the formula $\text{TeMe}_3 \cdot \text{O} \cdot \text{TeMeO}$, which reacts with hydriodic acid to give colourless trimethyltelluronium iodide (I) and a feebly acid substance, also colourless, *methyl hydroxytellurium oxide (telluracetic acid)* (II), or one of its anhydro-derivatives. The two products (I and II) are easily separated from each other, and the latter is readily converted by excess of hydriodic acid into *methyltelluronium tri-iodide* (III), an indigo-coloured crystalline substance, hydrolysable by hot water

but broadly non-polar in character. These two iodides readily unite, when mixed in molecular proportion in acetone solution, to give Vernon's β -di-iodide, obtained as magnificent greenish-black spangles identical with those produced on treating the aqueous β -base with hydriodic acid. The changes involved are :

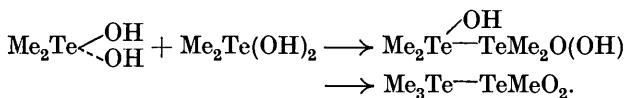


The change of the α - to the β -base probably takes place through an anhydride (IV) of the α -base by a molecular rearrangement almost identical with those of the pinacol-pinacolin type; *e.g.*,



but the mechanism involved in the migration of the methyl group is of course still obscure. The migrating group has to pass between two atoms not joined together directly, as they are in the carbon series, but bridged by oxygen. Strict analogy with pinacol would demand a formula $\text{Me}_3\text{Te}\cdot\text{TeMeO}$ for the β -base, and reductive changes would then have to be presumed with halide acids—the formation of the β -compounds being accompanied by that of other substances. Evidence in support of such an hypothesis has been sought but not obtained.

The remaining alternative is to represent the β -base by the formula $\text{Me}_3\text{Te}\cdot\text{TeMeO}_2$, a structure which could only result by the preliminary migration of a hydroxyl ion thus :



Such a substance might be converted by hydriodic acid into TeMe_3I and the tellurone, TeHMeO_2 ; and the latter would then have to be regarded as isomerising to the tellurinic acid derivative, $\text{TeMeO}(\text{OH})$. On the whole, this alternative view of the structure of the β -base is considered to be less probable than that previously suggested.

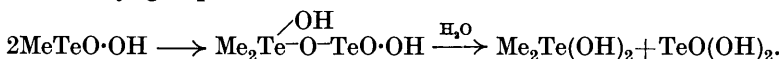
If the view that the formation of the β -base involves a migration of a methyl group is correct, similar changes may be sought in, *e.g.*, the silicon, germanium, tin, and lead series of alkyl and aryl halides and their bases. The occurrence of such changes may indeed account for the fact that compounds of the type MR_2X_2 ($\text{X} =$

halogen) are less readily obtained (through, *e.g.*, the Grignard reaction) than are those of the type MR_3X when intermediate hydroxylation is involved in the method of isolation.

Another crystalline, deeply coloured, complex *iodide* was isolated (see Experimental) in small quantities during the present work. This was $Me_3TeI, 2Me_2TeI_2$ (VI), which forms permanganate-coloured crystals. It is less stable than the " β -di-iodide" towards organic solvents.

An examination of the behaviour of the β -base with hydrobromic acid confirmed the previous deduction as to its nature. Colourless, crystalline *trimethyltelluronium bromide*, $TeMe_3Br$ (VII), was produced, together with a white substance identical with (II), which, on treatment with hydrobromic acid, yielded a yellow crystalline substance, *methyltelluronium tribromide*, $TeMeBr_3$ (VIII), soluble in ether. These two bromides, (VII) and (VIII), combined together in molecular proportion to give Vernon's " β -dibromide," identity being proved by a mixed melting point and a comparison of the general properties of the substances prepared in the two ways.

A small proportion of the α -base always accompanied the freshly isolated telluracetic acid, and the proportion of α -base increased when the product was kept in a desiccator for some weeks. It is probable, therefore, that telluracetic acid tends continually to change to a mixture of the α -base and tellurous acid, by the further wandering of a methyl group :



This is borne out by the fact that telluracetic acid, like the α -base and the α -dihalides, has a persistent odour of dimethyl telluride.

The α -base therefore tends towards an ultimate degradation to the most acid and the most basic substance possible, *viz.*, tellurous acid and trimethyltelluronium hydroxide :



Mixed " β -Dihalides."—To answer a possible objection that the " β -dihalides" might be formed by a rearrangement according to the equation $TeMe_3X + TeMeX_3 = 2TeMe_2X_2$, it was sought to prepare " β -dihalides" containing mixed halogens. This object was readily achieved. The appearance and properties of the mixed " β -dihalides" show that they belong to the same family as Vernon's β -dihalides, with which they form a series showing gradation of colours in crystals deposited, under uniform conditions, from acetone-chloroform solution. They are homogeneous substances, unaltered by further crystallisation. The series was :

$\text{TeMe}_3\text{I}, \text{TeMeI}_3$: purple-black, with green lustre ;
 $\text{TeMe}_3\text{Br}, \text{TeMeI}_3$: purple-red, with golden lustre ;
 $\text{TeMe}_3\text{I}, \text{TeMeBr}_3$: orange-brown ;
 $\text{TeMe}_3\text{Br}, \text{TeMeBr}_3$: yellow.

It is clear that the halogens of both components contribute to the colour of each salt, even although the components TeMe_3X are themselves colourless. The colour, however, is seen to be governed mainly by the halogens of the component TeMeX_3 , which are in excess.

The components reacted to form the salts when ground together even in the absence of solvents. This and the foregoing observations with regard to the colour changes show that the TeMe_3X components possess each a mobile halogen atom, probably functioning as a mobile anion ; and it becomes highly probable that the salts are correctly represented by the general formula $\text{Me}_3\text{Te}^+ \cdots \bar{\text{TeMeX}}_4$, equivalent to the co-ordination formula $[\text{Me}_3\text{Te}]\text{TeMeX}_4$, in which all the halogens and alkyl groups are covalently linked to tellurium. The negatively charged tellurium atom is thus associated with 58 electrons, if singlet linkings are assumed to be absent.

This view received support from the fact that a mixture * of acetone solutions containing equimolecular proportions of the " β -diiodide " and potassium iodide, respectively, gives a precipitate of pure trimethyltelluronium iodide. The red filtrate, diluted with chloroform, gives a black *substance* which is probably the salt $[\text{TeMeI}_4]^+\text{K}^-$, since it is dissociated by moisture into potassium iodide and methyltelluronium tri-iodide.

Vernon's molecular-weight determinations of his β -dihalides in acetone and in nitrobenzene gave figures which were considerably higher than those demanded by his theory in the case of the iodide and the bromide, but not for the chloride. These results indicate that the salts are more readily ionised when $\text{X} = \text{Cl}$ than when $\text{X} = \text{Br}$ or I . Conductivity measurements of the salts in certain organic solvents are being carried out.

A less probable alternative general formula for the " β -dihalides " is $[\text{Me}_3\text{Te}^+ \cdot \bar{\text{TeMeX}}_3]\bar{\text{X}}$, which differs from the first formula only as regards the position taken up by a single electron.

It was observed that such halides as ferric chloride and stannic bromide form coloured salts with trimethyltelluronium bromide or iodide. This suggests that there may be some analogy between the tellurium " β -dihalides " and the salts which the trisacetylacetone silicon, germanium, and titanium halides form with metallic chlorides,

* The author is indebted to Dr. N. V. Sidgwick for suggesting this test.

e.g., $[\text{SiA}_3]\text{AuCl}_4$, $[\text{TiA}_3]\text{FeCl}_4$, $[\text{GeA}_3]\text{CuBr}_2$. The possibility is thus presented of being able to replace the supposedly chelate acetyl-acetone radical (A) of the latter salts by univalent alkyl or aryl groups.

The assignment of a detailed formula to the triple salt (VI) must await further experimental evidence, but it may be noted that a salt of similar type occurs in the germanium series, *viz.*, $\text{GeA}_3\text{Br}_2\cdot 2\text{CuBr}$ (Morgan and Drew, J., 1924, **125**, 1261).

The α -dihalides possess marked solubility in light petroleum and other non-hydroxylic solvents, and are therefore to be regarded as distinctly non-polar substances, which, however, are capable of becoming ionised under exceptional conditions. If certain oxygen-containing radicals, such as HSO_4 and NO_3 , were substituted for X, the resulting compounds would probably be typically polar (*e.g.*, $\text{Me}_2\text{Te} \begin{matrix} \text{SO}_4\text{H} \\ \diagdown \\ \diagup \\ \text{SO}_4\text{H} \end{matrix}$), as first pointed out by the author (J., 1926, 3059).

The α -dihalides show normal molecular weights in benzene and in acetone. They are reduced to dimethyl telluride by alkali bisulphites, and are regenerated from the telluride by the direct addition of halogens. These and other experimental results establish fairly conclusively a monomeric formula for the α -dihalides.

The central fact which results from the present work is, therefore, that the supposed isomerism of the dimethyltelluronium dihalides has no existence; and the same conclusion may be presumed to obtain for the diethyl and other homologues. Tellurium has, in all probability, not a plane, but a tetrahedral distribution of valencies.

EXPERIMENTAL.

The α -di-iodide, TeMe_2I_2 , was prepared in the usual manner, and was recrystallised from chloroform, in which, contrary to Vernon's statement, it is quite stable (Found : C, 5.84; H, 1.46. Calc. : C, 5.84; H, 1.47%). It melts at 130° .

The β -base was prepared from this di-iodide as described by Vernon. The change of the α - to the β -base occurs in a vacuum at 95° , and the crystals of the latter appear to be stable for at least an hour at this temperature. When the filtered solution was treated with hydriodic acid, the precipitate obtained was manifestly non-homogeneous, a black tar (subsequently solidifying) and red crystals separating at different stages. The whole, when dissolved in acetone and precipitated by chloroform, gave glistening crystals of Vernon's β -di-iodide, which were either (a) deep purplish-red (Found : C, 6.04; H, 1.61%) or (b) bronzed greenish-black (Found : C, 5.97; H, 1.78%). Since the two varieties can be obtained from the same solution by precipitation under slightly different conditions, they

are probably the same substance. Each gives a reddish-purple streak, and the purple powder becomes black (decomposition) between 80° and 85° . The substance was almost insoluble in chloroform and most non-hydroxylic solvents.

When the β -di-iodide (1 part) was warmed with aqueous sodium carbonate (0.78 part), a chocolate-coloured precipitate (A) was produced, which, when dissolved in boiling water and precipitated by hydriodic acid, gave a black substance. The latter, extracted with warm chloroform, yielded a small quantity of the pure α -di-iodide. The filtrate from (A), on the addition of hydriodic acid, gave a black precipitate (B). This was removed, and the filtrate slowly deposited a beautifully crystalline *substance* (VI), resembling potassium permanganate in colour and partly soluble in hot chloroform (Found: C, 7.47; H, 1.94. $\text{TeMe}_3\text{I}_2\cdot 2\text{TeMe}_2\text{I}_2$ requires C, 7.48; H, 1.89%). The black *substance* remaining from (B) could not be crystallised. It was dried and analysed (Found: C, 5.3; H, 1.35. $\text{TeMe}_3\cdot\text{O}\cdot\text{TeI}_3$ requires C, 5.2; H, 1.3%).

Small quantities of the α -di-iodide are also produced when the β -di-iodide is treated with boiling water alone, or with aqueous potassium metabisulphite, and then with hydriodic acid. This is probably due, not to reversion of the β -base to the α -base, but to one of the mechanisms already discussed. A small quantity of tellurium tetraiodide also appears to be formed by the action of hot water.

The β -base was next prepared on a larger scale, and precaution was taken, by twice evaporating the filtered solution in a vacuum, to obtain it free from α -base. A portion tested with hydriodic acid gave the usual blackish-red precipitates, which yielded the pure β -di-iodide on recrystallisation. Finally the β -base (from 5 g. of α -di-iodide) was dissolved in about 30 c.c. of water and the vigorously stirred solution was treated with freshly distilled, diluted, colourless hydriodic acid (4.6 c.c. of 11.4% HI required), added drop by drop until the liquid seemed nearly neutral to litmus. Each drop produced a red precipitate, which redissolved when vigorously shaken, leaving the solution colourless. A few black and white specks separated and were removed. The liquid, left in a vacuum over sulphuric acid for 1—2 hours, gave glistening colourless crystals of almost pure trimethyltelluronium iodide (I), of which two crops were obtained (total, 0.69 g.) (Found: C, 12.06; H, 2.98. Calc.: C, 12.03; H, 3.00%). This crystallised readily from hot water in long needles or in large flat prisms. It decomposed slowly above 240° , and disappeared rapidly at 248° , forming probably dimethyl telluride and methyl iodide. Its aqueous solution was neutral to litmus and gave no coloration or precipitate, with hydrochloric acid or with colourless hydriodic acid.

The filtrate from this substance, when allowed to evaporate to dryness in the desiccator, gave an almost colourless, crystalline cake (1.30 g.). This was a mixture of the foregoing substance with a less soluble substance, which, however, tends to remain in supersaturated solution when once dissolved. The remaining trimethyltelluronium iodide was therefore removed from the mixture by gradual extraction with small quantities of hot water. The residue of white powder consisted of an *anhydride* of *methyl hydroxytellurium oxide* (*telluracetic acid*) (II), which could not be obtained pure. It appears to exist in several states of complexity, samples showing varying solubility in water. In aqueous solution, however, all were neutral to litmus, gave no precipitate with silver nitrate, and were reduced by potassium bisulphite to dimethyl ditelluride. Three separate preparations were analysed (Found : C, 7.6, 7.8, 7.7; H, 2.3, 2.0, 2.3. $\text{TeMeO}\cdot\text{O}\cdot\text{TeMeO}$ requires C, 7.2; H, 1.8%). The substance, which had a persistent odour, did not melt but became gradually black above 230° . It was dissolved in boiling water and into the clear cooled solution was stirred colourless hydriodic acid drop by drop, until the liquid was faintly yellow. A bright scarlet precipitate of *methyltelluronium tri-iodide* (III) was continuously produced, changing in a few seconds to a stable purplish-chocolate form. The dried crystalline powder (Found : C, 2.38; H, 0.65; I, 72.4. TeMeI_3 requires C, 2.29; H, 0.57; I, 72.8%) closely resembled pure indigo in appearance. It dissolves in acetone or ether, giving bright red solutions, and from the former it is slowly precipitated by chloroform, as purple-black needles. It is only sparingly soluble in chloroform or glacial acetic acid. It is hydrolysed by boiling water or dilute hydriodic acid and is reprecipitated on cooling. It slowly decomposes above 100° and evolves gas near 130° and again at 180° (melting), leaving a black residue : much of its iodine is liberated in the free state when it is heated in oxygen.

Synthesis of Vernon's β -Di-iodide.—Trimethyltelluronium iodide and methyltelluronium tri-iodide were intimately mixed in exactly molecular proportion. Both dissolved on being warmed with a little acetone, although the former alone is insoluble in that solvent. The red solution, diluted with chloroform, gave at once the pure β -di-iodide in lustrous greenish-black scales or thin hexagonal plates (Found : C, 5.91; H, 1.52. Calc. : C, 5.84; H, 1.47%). From the mother-liquor a small further crop of the β -di-iodide was obtained in the purple-red form. The total yield seemed to be almost quantitative. Both forms, when powdered, became black at about 83° , and were in every respect identical with the forms obtained directly from the β -base.

Action of Hydrobromic Acid on the β -Base.—When the β -base (from 10 g. of α -di-iodide) was dissolved in 20 c.c. of water and 7.2 c.c. of 9.8% hydrobromic acid were gradually added, a white precipitate (A) formed which redissolved completely at first but only partly later. The clear filtrate, concentrated in a vacuum to a syrup, yielded large crystals of *trimethyltelluronium bromide* (VII) (Found: C, 14.32; H, 3.66; Br, 31.38. TeMe_3Br requires C, 14.26; H, 3.57; Br, 31.66%), together with a white amorphous powder (B).

Trimethyltelluronium bromide is readily soluble in cold water but almost insoluble in organic solvents. It separates from water or aqueous alcohol in massive, transparent, colourless tablets, slowly decomposing between 250° and 280°. The neutral solution in water contains bromide ions and gives no precipitate or coloration with colourless hydriodic acid. The compound unites with ferric chloride, giving a complex salt which crystallises in salmon-coloured needles. It gives a complex salt also with stannic bromide.

The powders (A and B), when dissolved in hot water, treated with hydrobromic acid, and extracted with ether, gave *methyltelluronium tribromide* (VIII) (Found: C, 3.07; H, 0.78; Br, 62.9. TeMeBr_3 requires C, 3.14; H, 0.79; Br, 62.7%), yellow needles easily soluble in ether or hydrobromic acid, but hydrolysed by water. The substance becomes discoloured from about 140°, rapidly near 150°, and the dark mass melts to a black effervescing tar at 156°. The yellow solution in acetone is not precipitated by chloroform.

The crude powders (A and B), which consist of an anhydride of methyltellurium trihydroxide, contain also a small proportion of dimethyltellurium oxide or its oxybromide, since small amounts of the α -dibromide (colourless crystals, m. p. 96—97°, readily soluble in ether. Found: C, 7.6; H, 1.9. Calc.: C, 7.6; H, 1.9%) are produced by the action of hydrobromic acid.

Synthesis of Vernon's β -Dibromide.—The trimethyl bromide and the methyl tribromide combined when dissolved in equimolecular proportion in a little acetone, the yellow solution giving, on dilution with chloroform, lustrous yellow spangles (Found: C, 7.61; H, 1.97. Calc.: C, 7.56; H, 1.89%), m. p. 142° (decomp.; softening from 136°), unchanged on admixture with the β -dibromide prepared as described by Vernon. That author described the colour of this substance as "orange," but the crystals obtained from acetone-chloroform solution are always sulphur-yellow.

Mixed " β -Dihalides."—The following *compounds* were prepared from their constituents, precisely as described above for the β -di-iodide and β -dibromide:

(1) $\text{TeMe}_3\text{I}, \text{TeMeBr}_3$, lustrous, orange-brown, flat needles, forming felted masses; m. p. 120° (decomp.) with darkening and

softening from 115° (Found: C, 7.18; H, 1.78. $\text{Te}_2\text{Me}_4\text{Br}_3\text{I}$ requires C, 7.04; H, 1.76%). It was unaltered by recrystallisation from ethyl alcohol (Found: C, 7.3; H, 1.9%).

(2) $\text{TeMe}_3\text{Br}, \text{TeMeI}_3$, dark, purple-red spangles with golden lustre (Found: C, 6.39; H, 1.59. $\text{Te}_2\text{Me}_4\text{BrI}_3$ requires C, 6.19; H, 1.55%): this does not melt, but becomes black below 90° . When kept for a few weeks, the crystals change to a purple form, but recrystallisation from ethyl alcohol restores the original form.

Action of Potassium Iodide on the " β -Di-iodide."—Potassium iodide and the β -di-iodide in molecular proportion were dissolved separately in acetone, and the solutions mixed. Colourless crystals of pure trimethyltelluronium iodide were deposited at once (yield, 80%). The deep red filtrate was evaporated to dryness in a desiccator, the solid residue dissolved in a little cold acetone and filtered, and the filtrate fractionally precipitated with chloroform. The almost black precipitate at first obtained consisted of the salt $\overset{+}{\text{K}}[\overset{-}{\text{TeMeI}_4}]$ contaminated with free potassium iodide (Found: C, 1.2; H, 0.3. TeMeI_4K requires C, 1.7; H, 0.4%), but later, the proportion of free potassium iodide increased and the final mother-liquor contained free methyltelluronium tri-iodide. The complex potassium salt was insoluble in dry ether, but soluble in alcohol, giving a reddish-brown solution. It was easily dissociated by moist solvents.

The experimental findings of Vernon, so far as they have been examined here, are confirmed. Two observations in the literature, however, require modification, *viz.* (a) that the β -dihalides give dimethyl telluride on reduction, and (b) that the same tellurone, TeMe_2O_2 , is derived from both bases, and that halogen acids regenerate from it the β -dihalides.

Regarding (a), it was found that the product is an orange oil, with carbylamine odour quite distinct from that of dimethyl telluride. The oil is probably dimethyl ditelluride, produced from $\text{TeMeO}\cdot\text{OH}$ by the normal reaction, the other component of the β -base, $\text{TeMe}_3\cdot\text{OH}$, remaining unreduced.

As to (b), examination of the literature shows that the tellurone has never been characterised. Vernon may have mistaken for it a higher oxide of the β -base (new formulation), or a mixture of the true tellurone with this oxide. Further, in the formation of the tellurone from the α -base, the latter may have been partly transformed, by heating, to the β -base.

Finally, attempts to form molecular compounds from the following combinations of substances gave negative results:

- (1) TeI_4 and $\alpha\text{-TeMe}_2\text{I}_2$; (2) TeI_4 and TeMe_3I ;
- (3) $\text{TeI}_4 + \alpha\text{-TeMe}_2\text{I}_2 + 2\text{MeTe}_3\text{I}$.

On the other hand, α - TeMe_2I_2 and TeMe_3I combined together, in the presence of hydriodic acid containing iodine, to form a complex which crystallised in thin steel-blue needles, often several inches long. This substance, which melts to a purple liquid near 80° , evolves iodine when warmed with water. It has probably the formula $\text{TeMe}_3\text{I}, \text{TeMe}_2\text{I}_2, \text{TeMe}_2\text{I}_4$ [*i.e.*, it is a polyiodide of (VI)], but an exact analysis was not obtained (Found : C, 6.4; H, 1.7; I, 62.3. Calc. : C, 6.1; H, 1.5; I, 64.6%).

UNIVERSITY OF BIRMINGHAM,
EDGBASTON.

[Received, November 15th, 1928.
Revised, December 20th, 1928.]
