CCCCXXI.—*Studies of Valency. Part XII. Isomeric Derivatives of Diethyl Telluride.*

By FRANK LATHE GILBERT and THOMAS MARTIN LOWRY.

VERNON'S last paper on "Organic Derivatives of Tellurium" concludes as follows: "There is still much work to be done on this subject, and it would be of interest to find out whether other aliphatic derivatives, such as diethyltelluronium di-iodide, also exist in two isomeric forms. The reason that no further investigation is being undertaken is entirely due to the intolerable nature of tellurium and its derivatives" (J., 1921, **119**, 696). The present paper describes the completion of the investigation which Vernon contemplated, but was not able to undertake. This investigation has led to the discovery that diethyl telluride, like the dimethyl compound, yields two series of isomeric salts, and that these are derived from two isomeric bases, which are related to one another in precisely the same way as the α- and β-bases of the dimethyl series. This result was by no means a foregone conclusion, since the cyclic base prepared by Morgan and Burgess (this vol., p. 321) does not undergo isomeric change when evaporated to dryness (Gilbert and Lowry, this vol., p. 2658), although the di-iodide exists in two enantiotropic forms; and Mr. W. H. Mills has informed us that the diphenyl compound also shows no analogous transformation when treated in the same way as the dimethyl base. The isomeric derivatives now described therefore provide the first experimental justification for the view that the isomerism discovered by Vernon is not restricted to the methyl compounds, and may be a general property of the dialkyltelluronium bases and salts.

The salts in which this isomerism has been detected have been known for nearly a century. They were prepared by Wöhler (*Annalen*, 1840, **35**, 111; 1852, **84**, 73; 1855, **93**, 233) and by Mallet (*ibid.*, 1851, **79**, 223) by oxidising diethyl telluride to the dinitrate, $TeEt_2(NO_3)_2$, by the action of nitric acid. From this salt the chloride, bromide and iodide, the sulphate and oxalate, the oxide and the oxyhalides were obtained, but without any indication of isomerism or of isomeric change. Vernon prepared the α-di-iodide, $TeEt_2I_2$, by the action of ethyl iodide on metallic tellurium and analysed the product; it melted at 57°, whereas Wöhler gives the m. p. as 50°. He also prepared the base by the action of silver oxide on the iodide, and added that " If this base does not decompose when its solution is evaporated to dryness, but gives diethyltelluronium oxide, the existence of two haloid series would be highly probable." Our first attempt to verify this prediction gave rise to *diethyltellurone*, $TeEt_2O_2$, by spontaneous oxidation of the base, whereas the α- and β-dimethyl bases and Morgan's cyclic base are only oxidised to the tellurone by boiling with hydrogen peroxide; but by evaporating a solution of the α-base to dryness in an atmosphere of nitrogen, a substance was obtained which gave in aqueous solution quite different reactions towards silver nitrate and hydriodic acid and evidently contained the isomeric β-base. From this substance a characteristic series of β-salts was prepared.

The two series of isomeric salts correspond very closely with those of the dimethyl series. Thus the α-di-iodide differs from the β-compound in that it is freely soluble in chloroform, and can be converted into a tetra-iodide. The remarkable contrast which Vernon observed between the action of alkalis on the α- and β-salts was also repeated in the diethyl series. Thus, the α-di-iodide gave rise to an *oxyiodide*, $I[TeEt_2\cdot O\cdot TeEt_2]I$, although this was produced under a wider range of conditions than in the methyl series, since the same product was obtained when we tried to prepare the ethyl analogue of Vernon's beautifully crystalline α-dimethyltelluronium dioxyiodide. The β-di-iodide, on the other hand, was converted by the action of alkali into a salt having the characteristics and the approximate composition of a *triethyltelluronium iodide*, $TeEt_3I$.

A remarkable contrast is found in the fact that the α- and β-chlorides and bromides of the diethyl series are obtained as oils, whereas those of the dimethyl series are crystalline solids of fairly high melting point. A close analogy (comparable with that which has already been pointed out in connexion with the conductivities; this vol., p. 314) is found, however, in the trialkylstibine series, where the trimethylstibine dihalides are all solid, as is also the triethylstibine di-iodide, whereas the triethylstibine dichloride and dibromide are liquids.

Apart from this contrast in melting points, the physical properties of the diethyl compounds are in general such as we should have expected in the light of our observations on the dimethyl series. For instance, the absorption spectra of the iodides all show the twin maxima of the "iodoform band," and the bromides exhibit only a step-out. Again, measurements of molecular conductivity show that, when dissolved in water, the dihalides lose one atom of halogen by hydrolysis to the free acid, giving rise to hydroxy-halides, to which the general formula $[TeEt_2{\cdot}OH]X$ is assigned. The only compound of the group which has been isolated is, however, the α-oxyiodide, $I[TeEt_2{\cdot}O{\cdot}TeEt_2]I$. The hydroxy-halides are ionised more or less completely in aqueous solution, but are not hydrolysed even in dilute solutions from which the excess of acid has been removed. As in the methyl series, they are acid rather than alkaline in their reaction.

An interesting comparison can be made between the properties of the α- and the β-base. As in the dimethyl series, the β-base has a higher conductivity than the isomeric α-base, and it is also shown by potentiometric titrations to be stronger than the α-base during the first half of the process of neutralisation. At this stage, however, the curves cross, so that the β-base is seen to be weaker than the α-base after half-neutralisation. The crossing of the curves is due to the fact that, whilst the α-base gives a neutralisation curve of the normal type, the cürve for the β-base is inflected, exactly as in the case of the α-dimethyl base (this vol., p. 1997), although not to such a marked extent. The reappearance of this inflected curve in the case of the β-base, and the absence of any inflexion in the curve for the α-base, provide the most striking evidence of the persistent analogy between the methyl and ethyl series of compounds.

EXPERIMENTAL.

α-Diethyltelluronium Di-iodide.—Precipitated tellurium (crushed crystalline tellurium is less effective) is heated in Carius tubes for 10 days at 100° with ethyl iodide (2 mols.), the tubes being shaken every 12 hours. Very little pressure is developed, even at 100°, and there is no pressure when the tubes are opened. Since the compound has been found to decompose slightly during fusion, it would probably be better to heat at 40—50° during a period of perhaps 20 days, so that the compound is not prepared in the fused state. The di-iodide was extracted with hot chloroform (instead of with alcohol, as recommended by Vernon), filtered through a hot funnel to remove unchanged tellurium, and separated by rapid evaporation. It was obtained from alcohol in large brownish-red crystals, m. p. 57°; yield, about 20%. The final product was identical in all respects with a specimen left by Vernon.

The *α-tetraiodide*, $TeEt_2I_4$, was obtained as a black residue on mixing a violet solution of iodine and a yellow solution of the α-di-iodide in chloroform, and refluxing the mixture for one minute, the colour almost wholly disappearing; but some decomposition occurred in this process, giving rise to free iodine and tellurium. The α-tetra-iodide was also formed when hydriodic acid was added to a solution of the α-base, which had been partly oxidised by boiling with hydrogen peroxide for a few minutes, and then filtered from the resulting diethyltellurone. It melts at 98°, and loses iodine in the air, regenerating the α-di-iodide. (After reduction with sulphur dioxide and addition of nitric acid, Volhard's method gave I, 71. $TeEt_2I_4$ requires I, 73·2%).

The β-di-iodide does not combine with iodine under the conditions described above.

Preparation and Properties of the α-Base.—The α-base, which was described by Mallet as a colourless, crystalline mass, and by Wöhler as a white, amorphous mass, was prepared by grinding the solid α-di-iodide with fresh moist silver oxide, in exactly the same way as the corresponding dimethyl base. When hydriodic acid was added to the aqueous solution, the α-di-iodide was regenerated as a bright yellow precipitate, settling to a red solid. Silver nitrate gave a white precipitate, turning brown and then black. On evaporation to dryness at 100° under 15 mm. pressure, a colourless oily residue was left, which changed to a white non-crystalline solid when it was allowed to cool and to come in contact with cold water. This product, which was sparingly soluble in water and insoluble in organic solvents, decolorised permanganate and liberated violet fumes of iodine when warmed with concentrated hydriodic acid. Analysis showed that the α-base had been oxidised to *diethyltellurone*, $TeEt_2O_2$ (0·0254 g. gave 0·0147 g. Te when oxidised with aqua regia and reduced with sulphur dioxide and hydrazine hydrochloride: Te, 58·0. $TeEt_2O_2$ requires Te, 58·6%).

Preparation and Properties of the β-Base.—The β-base was obtained by evaporating a solution of the α-base to dryness at 100° under 15 mm. pressure in a stream of nitrogen. In order to dissolve it, a sealed tube of air-free water was broken inside the flask, which was then filled with nitrogen under atmospheric pressure. The β-base was then quite stable and resistant to oxidation, but was mixed with some unchanged α-base and some diethyltellurone. To purify it, hydriodic acid was added to the solution, and the mixed di-iodides were washed with a few drops of cold chloroform (in which the α-di-iodide is freely soluble); the pure β-di-iodide was then reconverted into the β-base by the action of silver oxide.

The β-base gives a faint white precipitate with silver nitrate, which turns black on boiling, but not in the cold. With hydriodic acid it gives a dark red precipitate of the β-di-iodide which settles to a purple solid; the presence of any α-base as impurity can be detected by the formation of a fine yellow precipitate which remains at the top of the beaker.

Preparation and Properties of the β-*Di-iodide*.—The β-*di-iodide* can be prepared in a crude form by the action of hydriodic acid on the crude β-base, and freed from the α-isomeride by washing with chloroform, in which it is almost insoluble. It can also be obtained (free from the α-isomeride) by the action of hydriodic acid on diethyltellurone. It separates from methyl alcohol in dark purple crystals, m. p. 42° (Found : I, 57·2. $TeEt_2I_2$ requires I, 57·9%). It is also readily soluble in acetone, but gives a lachrymatory vapour (possibly iodoacetone) when the solution is evaporated.

α- *and* β-*Dibromides*.—The α-dibromide was obtained by Wöhler as a pale yellow oil of high boiling point. We obtained it in a similar form (Found : Br, 46·2. Calc. for $TeEt_2Br_2$: Br, 46·4%), but found that it solidified when cooled with a freezing mixture of ice and salt. When freed from the mother-liquor and dried in a vacuum desiccator, the solid does not melt till + 24°, but it does not then resolidify on cooling. The β-*dibromide* was obtained as a yellow oil of deeper colour, and solidified to a glass at −12° (Found : Br, 46·0. $TeEt_2Br_2$ requires Br, 46·4%).

α- *and* β-*Dichlorides*.—The α-dichloride was prepared by Mallet, who distilled it without decomposition at a temperature too high to be measured. We obtained it as a colourless oil (Found : Cl, 27·0. Calc. : Cl, 27·6%) which froze to a glass in a freezing mixture at −12°, and melted again at −5°. The β-*dichloride* was also obtained as a colourless oil (Found : Cl, 27·8. $TeEt_2Cl_2$ requires Cl, 27·6%) which solidified in a freezing mixture and melted again at −10°.

Action of alkalis. (a) In order to prepare a "dioxyiodide," the α-di-iodide was ground up with a little concentrated ammonia, dissolved in the minimum quantity of water, and left to crystallise in a vacuum desiccator. Colourless crystals separated, which melted at 107° and turned red on exposure to air; but these were shown by analysis to be an α-*monoxyiodide*, to which the formula $I[TeEt_2{\cdot}O{\cdot}TeEt_2]I$ may be assigned (I, 39·0; calc., 39·5%). When the crystals were boiled with water and cooled, in order to convert the supposed "dioxyiodide" into a "monoxyiodide," the same product was obtained (I, 39·9; calc., 39·5%), but in a less pure form, since it melted at 104—106°. This was a sticky, orange-yellow precipitate, which resembled the yellow "monoxyiodide" of the methyl series; but, unlike the methyl compound, it did not lose its colour after long standing in contact with water; nor did it lose its colour when recrystallised from hot water.

(b) The product obtained by boiling the β-di-iodide with half an equivalent of sodium carbonate in concentrated solution, and then cooling, was a white precipitate, which was washed with a drop of ice-cold water. It had the properties of a *triethyltelluronium iodide*, since it did not change colour when exposed to acid fumes, and blackened without melting above 180°. It was appreciably soluble in water, but insoluble in organic solvents; it was therefore not easy to free it completely from sodium carbonate, the low percentage of iodine found on analysis thus being accounted for (Found: I, 35·9. $TeEt_3I$ requires I, 37·3%).

Action of mercury diphenyl. Vernon directs attention to the "almost unique" action of mercury diphenyl on α-dimethyltelluronium di-iodide and states that the interaction with the α-diethyl compound "does not take place in this curious manner." On mixing equimolecular solutions in chloroform of mercury diphenyl and of the α-di-iodide, $TeEt_2I_2$, the brown colour of the solutions became yellow, and after about 5 seconds a yellow precipitate was suddenly formed, very much as in the case of the dimethyl compound. This precipitate was a heavy, yellowish-green oil; when cooled to $-8°$, it solidified to a pale yellow, crystalline mass, and then remained solid up to 94°. (The α-methyl compound melts at 125°.) The addition compound is soluble in acetone, but does not crystallise well from this solvent. When boiled with chloroform or alcohol, it liberates a smell resembling that of carbylamine. Analysis showed that it contains two molecules of the di-iodide to one of mercury diphenyl [Found: Hg + Te, 36·3. $(TeEt_2I_2)_2,HgPh_2$ requires Hg + Te, 35·0%]. Mercury di-*p*-tolyl does not appear to interact with α-dimethyl- or α-diethyl-telluronium di-iodide.

Absorption Spectra.

The absorption spectra of the dimethyl series had been determined in specially dried alcohol in order to avoid hydrolysis (this vol., p. 308), but since Batley (*Trans. Faraday Soc.*, 1928, **24**, 438) has described a reaction between alcohol and iodine, it was thought preferable to measure the absorption spectra in a more inert solvent. They were therefore observed in *cyclo*hexane, which had been shaken with oleum and with sodium carbonate, dried, and fractionated.

The α-dihalides are readily soluble in *cyclo*hexane. The β-dihalides are only very sparingly soluble, but since only very dilute solutions were required, the concentrations of the saturated solutions were found to be sufficient. The extinction coefficients of the α- and β-di-iodides and of the α- and β-dibromides of the diethyl series were measured; but not those of the dichlorides or of the hydroxy-salts, which give only general absorption. For the purpose of comparison, the absorption spectra of α- and β-dimethyltelluronium di-iodides were also measured in *cyclo*hexane.

The most important values of λ and of log ε are set out in Table I, and the corresponding absorption curves are plotted in Fig. 1. The general results are very similar to those already recorded for solutions of the dimethyl salts in alcohol, but the absolute values of the extinction coefficients in *cyclo*hexane are higher than in ethyl alcohol; the wave-length of the head of the band is also shorter in every case.

FIG. 1.

Molecular extinction coefficients in cyclo*hexane.*

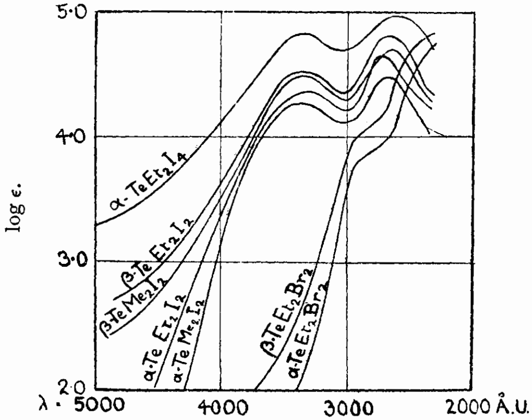


TABLE I.

Extinction Coefficients of Diethyltelluronium Dihalides.

α-TeMe$_2$I$_2$ $\lambda = 3400$ at $\log \epsilon = 4{\cdot}27$; $\lambda = 2680$ at $\log \epsilon = 4{\cdot}47$
β-TeMe$_2$I$_2$ $\lambda = 3360$ at $\log \epsilon = 4{\cdot}49$; $\lambda = 2640$ at $\log \epsilon = 4{\cdot}70$
α-TeEt$_2$I$_2$ $\lambda = 3350$ at $\log \epsilon = 4{\cdot}36$; $\lambda = 2700$ at $\log \epsilon = 4{\cdot}65$
β-TeEt$_2$I$_2$ $\lambda = 3350$ at $\log \epsilon = 4{\cdot}51$; $\lambda = 2670$ at $\log \epsilon = 4{\cdot}80$
α-TeEt$_2$I$_4$ $\lambda = 3350$ at $\log \epsilon = 4{\cdot}82$; $\lambda = 2630$ at $\log \epsilon = 4{\cdot}95$
α-TeEt$_2$Br$_2$ Step-out from λ 2900 to 2660 at $\log \epsilon = 3{\cdot}8$ to 4·0
β-TeEt$_2$Br$_2$ Step-out from λ 2900 to 2690 at $\log \epsilon = 4{\cdot}0$ to 4·2

Molecular Conductivities.

These were determined at 25° in cells of which the constants were 0·2240 and 0·1250 cm.$^{-1}$. Since the dihalides were difficult to dissolve and it was inadvisable to boil them with water, they were dissolved in the minimum quantity of cold ethyl alcohol and the solutions were diluted with cold conductivity water. The amount of alcohol in the most concentrated solution is shown in parentheses in Table II and was never more than 4%; and this, of course, is halved at each dilution. A correction, of $2\frac{1}{2}$ times the percentage of alcohol, was applied to the final conductivity values. The validity of this correction has already been demonstrated (this vol., p. 313).

The solutions of the bases were standardised by titration against $N/10$-hydrochloric acid with bromophenol-blue as indicator. Solutions of the hydroxyhalides were prepared by mixing equimolecular solutions of dihalide and base. The β-dichloride was not investigated, since after purification and analysis there was not sufficient material available.

The molecular conductivities at 25° are summarised in Table II. The behaviour of the salts is similar to that of the dimethyl salts, but there is some contrast in the behaviour of the bases. For instance, whilst the α-base has the same low conductivity as the corresponding methyl base, the β-base has a conductivity ranging from 8 to 16 units as compared with 34 to 37 for the β-base of the methyl series. The somewhat higher values recorded for the β-base prepared from α-base are doubtless due to traces of impurities in the solution. A solution of the crystalline oxyiodide, $I[TeEt_2{\cdot}O{\cdot}TeEt_2]I$, made up without the use of alcohol, gave molecular conductivities which were slightly less than twice the values recorded for the hydroxyiodide, exactly as was observed in the methyl series (this vol., p. 2006).

TABLE II.

Molecular Conductivities of Diethyltelluronium Compounds at 25°.

(Corrected for alcohol content.)

v =	256.	512.	1024.	2048.	4096.
(a) *Dihalides.*					
α-$TeEt_2Cl_2$ (1·5) *	505	514	520	524	529
α-$TeEt_2Br_2$ (3)	503	511	517	521	523
α-$TeEt_2I_2$ (4)	504	512	518	524	527
α-$TeEt_2I_4$ (4)	—	493	499	501	503
β-$TeEt_2Br_2$ (1·8)	507	514	521	527	528
β-$TeEt_2I_2$ (4)	506	512	517	524	529
(b) *Hydroxy-halides.*					
α-$TeEt_2(OH)Cl$ (0·3)	97	104	108	110	113
α-$TeEt_2(OH)Br$ (0·8)	100	104	107	109	114
α-$TeEt_2(OH)I$ (1·5)	98	100·5	102	107	111
α-$(TeEt_2)_2OI_2$ (0)	185	194	198	204	213
β-$TeEt_2(OH)Br$ (1)	104	104·5	106·5	110	112
β-$TeEt_2(OH)I$ (2)	99·5	102	104·5	107	109

v =	32.	64.	128.	256.	512.	1024.
(c) *Bases.*						
α-$TeEt_2(OH)_2$ ...	2·7	3·3	3·9	4·55	5·85	8·0
β-$TeEt_2(OH)_2$						
from α-base ...	10·5	11·4	12·6	13·5	15·1	—
from β-salt ...	8·6	9·5	10·5	12·8	—	—

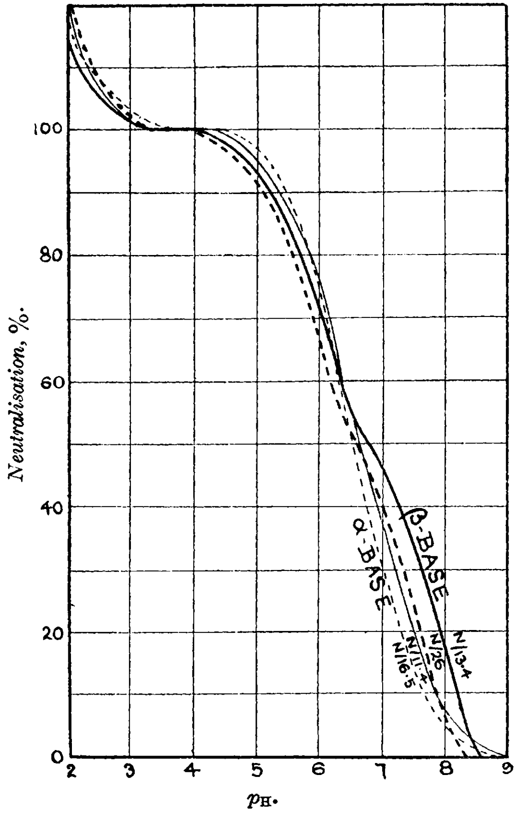
* The numbers in parentheses show the percentage of alcohol in the most concentrated solution.

Potentiometric Titrations.

These were carried out with a glass electrode, *N*-hydrochloric acid being used for the titration. The glass electrode had a very thin bulb, and gave about 56 millivolts per p_H. The potentials were checked by taking readings of an acid and an alkaline solution of known p_H every time a titration was made. Two curves for the α-diethyltelluronium base and two for the β-base (prepared in each case from the β-salt) are shown in Fig. 2, and some of the principal data are summarised in Table III.

Fig. 2.

Potentiometric titrations.



The curves for the α-base are quite normal; those for the β-base show an intermediate inflexion at 50% neutralisation, although of a less pronounced character than in the case of the methyl base. The inflexion at 100% neutralisation corresponds in each case with the formation of the hydroxyhalide, [TeEt$_2$OH]Cl, but there is no sign of the second hydroxyl being neutralised at 200% neutralisation. nor is there any indication of basic compounds apart from the inflexion in the curves for the β-base. The curve for the $N/16{\cdot}5$-solution of the α-base is on the acid side of that for the $N/11{\cdot}4$-solution, as might be expected; this is also true of the $N/26$- and $N/13{\cdot}4$-solutions of the β-base. An anomaly is found in the fact that the foot of the curve for the α-base is on the alkaline side of that for the β-base, which has a higher molecular conductivity; but we do not attach any importance to this anomaly, since it disappears after 2 or 3 drops of acid have been added.

The data cited in Table III show that the dissociation constant K_b of the α-base is given by $-\log K_b = 7{\cdot}5$. The strength of the β-base cannot be deduced from the $p_{\rm H}$ at half-neutralisation, since the curve is inflected at this point, but it can be deduced from the relation $-\log K_b = \log\{(1-x)/x\} + p_{K_w} - p_{\rm H}$, where x is the fraction of base neutralised. The $p_{\rm H}$ at 25% neutralisation then gives $-\log K_b = 6{\cdot}7$. The β-base is therefore stronger than the α-base, which is in accordance with the conductivity measurements. The $p_{\rm H}$ at 75% neutralisation shows that the dissociation constant of the basic salt formed at 50% neutralisation of the β-base is $-\log K_b = 7{\cdot}62$.

The relationship between the dimethyl- and the diethyl-telluronium bases is as follows: the two α-bases are of exactly the same strength, $-\log K_b = 7{\cdot}5$; the true β-methyl base, $-\log K_b = 6{\cdot}2$, is stronger than the β-ethyl base, $-\log K_b = 6{\cdot}7$; but the basic salt 2TeEt$_2$O,HCl, $-\log K_b = 7{\cdot}62$, is a stronger base than the basic salt 2TeMe$_2$O,HCl, $-\log K_b = 8{\cdot}7$.

TABLE III.

Potentiometric Titrations.

		$p_{\rm H}$.					Range of $p_{\rm H}$ 98% to 102%.
Neutralisation.		Initial.	50%.	100%.	98%.	102%.	
α-Base	$N/16{\cdot}5$	8·90	6·5	3·8	4·88	3·14	1·74
α-Base	$N/11{\cdot}4$	9·08	6·55	3·8	4·72	2·86	1·86
β-Base	$N/26{\cdot}0$	8·30	6·60	3·64	4·30	3·00	1·30
β-Base	$N/13{\cdot}4$	8·60	6·78	3·63	4·48	2·86	1·62

Summary.

1. α-Diethyltelluronium di-iodide yields an α-base, which is converted into an isomeric β-base when the aqueous solution is evaporated to dryness in a vacuum.

2. From the β-base a series of β-salts can be prepared. The two series of salts differ in their behaviour towards alkali, since the

α-iodide gives a colourless monoxyiodide, whereas the β-iodide gives a triethyltelluronium salt; and a tetra-iodide could only be prepared from the α-base.

3. The β-base is stronger than the α-base, and gives an inflected potentiometric curve, as in the methyl series.

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