69. *The Oxidation of Certain Alkyl Tellurides.*

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From di-*n*-butyl telluride and the ethyl and the *l*-menthyl ester of *n*-butyltelluroacetic acid, by interaction with alkyl halides or by oxidation under acid conditions, telluronium compounds are obtained which are readily soluble in organic solvents and have definite melting points. Oxidation of the three tellurides under neutral conditions gives *n*-butyltellurinic acid or products which contain this acid associated with telluroxides: these are all insoluble or only sparingly soluble in organic solvents and have no true melting points, but decompose between 180° and 220°. Oxidation of *l*-menthyl tellurodiacetate by neutral hydrogen peroxide gives a compound of the telluronium type, formed by combination of the telluroxide with hydrogen peroxide.

The decomposition of aliphatic telluroxides which results in the formation of *n*-butyltellurinic acid is discussed. The suggestion is made that this acid exists as polymerides, and that telluroxide molecules may be associated with these polymerides in such a way as to prevent the decomposition of the telluroxide.

Di-*n*-butyl telluride, prepared by a method similar to that used by Tschugaev and Chlopin (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 364) for the preparation of alkyl selenides, combines with methyl iodide and with certain substituted alkyl bromides to give crystalline telluronium halides, (XII)—(XV) in the table. By thermal decomposition of (XIII) and (XIV) the unsymmetrical aliphatic tellurides *ethyl* n-*butyltelluroacetate* and l-*menthyl* n-*butyltelluroacetate* respectively are obtained, which give the crystalline *telluronium bromides* (XVI) and (XVII) by combination with ω-bromoacetophenone.

Like tellurodiacetic and ditellurodiacetic acid (Morgan and Drew, J., 1925, **127**, 531), dimethyl telluride (Vernon, J., 1920, **117**, 889), di-*p*-anisyl ditelluride (Morgan and Kellett, J., 1926, 1080), *cyclo*telluropentane (Morgan and Burgess, J., 1928, 321), and *cyclo*tellurobutane (Morgan and Burstall, J., 1931, 180), these two unsymmetrical tellurides, as well as di-*n*-butyl telluride, are oxidised when exposed to air in the homogeneous state or in solution. They are also readily oxidised by nitric acid or by hydrogen peroxide.

The compositions of the oxidation products isolated are given in the table. In most cases, oxidation by air or hydrogen peroxide under neutral conditions gives the expected telluroxide associated with *n*-butyltellurinic acid, but only n-*butyltellurinic acid* (I) was isolated from the products of the action of air, or of hyperol (urea perhydrate) in ethyl-alcoholic solution, on *l*-menthyl *n*-butyltelluroacetate.

When the tellurides are oxidised under acid or alkaline conditions, simple derivatives of quadrivalent tellurium are obtained. For example, the oxidation of di-*n*-butyl telluride and of *l*-menthyl *n*-butyltelluroacetate by dilute nitric acid yields the corresponding *hydroxy-nitrates* (X), (XI), and alkaline hydrogen peroxide oxidises di-*n*-butyl telluride to the *dihydroxide* (VIII). The oxidation of *l*-menthyl *n*-butyltelluroacetate by benzoyl peroxide gives a compound which may be formed by the union of one molecule of *l*-menthyl *n*-butyltelluroxyacetate with two molecules of benzoic acid. Our analyses of this compound suggest that it is formed with elimination of water, and that it is the *dibenzoyl* derivative of the dihydroxide of *l*-menthyl *n*-butyltelluroacetate (IX), analogous to the diacetyldiarylselenonium compounds described by Foster (*Rec. trav. chim.*, 1935, **54**, 446).

Oxidation Products and Telluronium Compounds derived from Di-n-*butyl Telluride and the Ethyl and* l-*Menthyl Esters of* n-*Butyltelluroacetic Acid.*

From	Reagent.	Product.		Decomp. temp. or m. p.
$Bu\cdot Te\cdot CH_2\cdot CO_2C_{10}H_{19}$	air	$Bu\cdot TeO\cdot OH$	(I)	decomp. 220°
,,	hyperol	,,		,,
$TeBu_2$	air	$TeBu_2O,3Bu\cdot TeO\cdot OH$	(II)	decomp. 180
$Bu\cdot Te\cdot CH_2\cdot CO_2Et$	,,	$Bu\cdot TeO\cdot CH_2\cdot CO_2Et,2Bu\cdot TeO\cdot OH$	(III)	decomp. 185
,,	H_2O_2	,,		,,
(XI)	$NHEt_2$	$Bu\cdot TeO\cdot CH_2\cdot CO_2H,2Bu\cdot TeO\cdot OH$	(IV)	decomp. 210
$Bu\cdot Te\cdot CH_2\cdot CO_2C_{10}H_{19}$	H_2O_2	$Bu\cdot TeO\cdot CH_2\cdot CO_2C_{10}H_{19},Bu\cdot TeO\cdot OH$	(V)	decomp. 210
$TeBu_2$	,,	$2TeBu_2O,Bu\cdot TeO\cdot OH$	(VI)	decomp. 180
(V)	HNO_3	$Bu\cdot TeO\cdot O\cdot TeBu(NO_3)\cdot CH_2\cdot CO_2C_{10}H_{19}$	(VII)	decomp. 130
$TeBu_2$	alkaline H_2O_2	$TeBu_2(OH)_2$	(VIII)	decomp. 120
$Bu\cdot Te\cdot CH_2\cdot CO_2C_{10}H_{19}$	benzoyl peroxide	$Bu\cdot Te(O\cdot COPh)_2\cdot CH_2\cdot CO_2C_{10}H_{19}$	(IX)	m. p. 133
$TeBu_2$	HNO_3	$TeBu_2(OH)\cdot NO_3$	(X)	m. p. 84
$Bu\cdot Te\cdot CH_2\cdot CO_2C_{10}H_{19}$	,,	$Bu\cdot Te(OH)(NO_3)\cdot CH_2\cdot CO_2C_{10}H_{19}$	(XI)	m. p. 42
$TeBu_2$	MeI	$TeMeBu_2I$	(XII)	m. p. 159
,,	$CH_2Br\cdot CO_2Et$	$TeBu_2Br\cdot CH_2\cdot CO_2Et$	(XIII)	m. p. 63
,,	$CH_2Br\cdot CO_2C_{10}H_{19}$	$TeBu_2Br\cdot CH_2\cdot CO_2C_{10}H_{19}$	(XIV)	m. p. 90
,,	$CH_2Br\cdot COPh$	$TeBu_2Br\cdot CH_2\cdot COPh$	(XV)	m. p. 87
$Bu\cdot Te\cdot CH_2\cdot CO_2Et$	,,	$TeBuBr(CH_2\cdot CO_2Et)\cdot CH_2\cdot COPh$	(XVI)	m. p. 89
$Bu\cdot Te\cdot CH_2\cdot CO_2C_{10}H_{19}$	,,	$TeBuBr(CH_2\cdot CO_2C_{10}H_{19})\cdot CH_2\cdot COPh$	(XVII)	m. p. 106

On account of their limited solubility, *n*-butyltellurinic acid and the complex products (II)—(VI) cannot be recrystallised. It is, however, suggested that (II)—(VI) are compounds, not only on account of the improbability that mixtures of the two components would separate in an amorphous infusible state in consistently simple proportions, but also because they cannot be readily separated into telluroxides and *n*-butyltellurinic acid. For example, (V) loses up to 40% in weight on trituration with aqueous sodium carbonate, but no precipitate is obtained on neutralisation or acidification of the extract. When (V) is treated with nitric acid, the *n*-butyltellurinic acid which it contains is not converted into a soluble nitrate. A new substance is obtained which contains equimolecular proportions of *l*-menthyl *n*-butyltelluroxyacetate, *n*-butyltellurinic acid, and nitric acid and is probably best formulated with elimination of water, as the l-*menthyl* ester of *n*-butyl *n*-butyltellurinyltelluretine nitrate (VII), analogous to the dibenzoyl derivative (IX). The action of diethylamine on the hydroxy-nitrate (XI) also indicates that telluroxides cannot be isolated readily from the compounds which they form with acids. The removal of nitric acid by the amine is accompanied by hydrolysis and oxidation of the telluroxide, the product of the reaction being a substance (IV) which contains *n*-butyltelluroxyacetic acid and *n*-butyltellurinic acid.

The simple telluronium compounds (IX)—(XVII) melt between 42° and 159° and are all readily soluble in one or more solvents. The complex compounds (II)—(VI), on the other hand, have no true melting points, but decompose between 180° and 220° and are insoluble or only sparingly soluble in most organic solvents. *n*-Butyltellurinic acid (I), (II), and (IV) are sparingly soluble only in boiling ethyl alcohol, (III) and (VI) are somewhat more soluble in boiling ethyl alcohol [the solution of (VI) gelates on cooling], and only (V) is soluble in cold ether, chloroform and carbon disulphide.

n-Butyltellurinic acid, in its infusibility and sparing solubility, resembles phenyltellurinic acid (Lederer, *Ber.*, 1915, **48**, 1345), but is in contrast to the recorded alkylsulphinic and -seleninic acids, all of which melt below 140° and are readily soluble in a number of organic solvents. The properties of *n*-butyltellurinic acid suggest that it exists as a polymeride. Two modes of polymerisation present themselves, hydrogen-bond formation, and the formation of a covalency between the telluroxide oxygen of one molecule and the tellurium of another. The latter structure, in harmony with the infusibility of the acid, is the more likely, involving the expansion of the outer shell of the tellurium atom to ten electrons. Patry (*Compt. rend.*, 1935, **201**, 71) has concluded that telluric acid

(H_2TeO_4) exists as polymerides; this structure, if confirmed, would be analogous to that now postulated for *n*-butyltellurinic acid.

The formation of tellurinic acids in the oxidation of dialkyl tellurides is due to the instability of the telluroxides which are the primary oxidation products. These decompose into butane-1-tellurol and an aldehyde, which in the presence of excess of the oxidising agent are converted into *n*-butyltellurinic acid and a carboxylic acid respectively (*n*-butyric acid was isolated as a by-product of the oxidation of di-*n*-butyl telluride by hydrogen peroxide). Many aliphatic sulphoxides and most aliphatic selenoxides decompose in a similar manner (Edwards, Gaythwaite, Kenyon, and Phillips, J., 1928, 2293; Larsson and Jönsson, *Ber.*, 1934, **67**, 2003). Sulphinic and seleninic acids can be isolated in simple forms, but the lesser stability of quadrivalent tellurium compounds would cause monomeric alkyltellurinic acids to decompose by further enolisation. As a polymeride, telluric acid cannot enolise, and hence is sufficiently stable to be isolated.

The formation of (II)—(VI), by oxidation under neutral conditions, is then to be attributed to the instability of alkyl telluroxides, which results in the formation of *n*-butyltellurinic acid, and to the tendency of the tellurinic acid so formed to polymerise and to become associated with the telluroxide by oxygen–tellurium bonds. The association of a number of molecules in this way, either by ring formation or by extensive linear polymerisation, would prevent the enolisation which leads to decomposition of the telluroxides and tellurinic acid. Alkaline or acid conditions of oxidation result in the formation of the dihydroxide (VIII), or derivatives of dihydroxides (IX), (X), (XI), in which enolisation is impossible, so these compounds are comparatively stable and of simple constitution.

The present experiments suggest that dialkyl telluroxides cannot be isolated from the oxidation products of dialkyl tellurides; few well-characterised dialkyl telluroxides are described in the literature. The dimethyl and diethyl telluroxides described by Mallet (*Annalen*, 1851, **79**, 223) and Wohler and Dean (*Annalen*, 1855, **93**, 235) were probably dihydroxides, since they were obtained by the action of silver oxide on the corresponding dihalides in aqueous solution, and the recorded properties of *cyclo*tellurobutane 1-oxide (Morgan and Burgess, J., 1931, 182) are consistent with the suggestion that it was a complex substance analogous to those described above. Diaryl selenoxides (Edwards, Gaythwaite, Kenyon, and Phillips, *loc. cit.*) are more stable than dialkyl selenoxides and it is therefore likely that telluroxides of the diaryl series would be more stable than those of the dialkyl series. Lederer (*Annalen*, 1912, **391**, 326; *Ber.*, 1916, **49**, 334, 1071, 1615, 2552; 1920, **53**, 1674) obtained eleven diaryl telluroxides which had melting points ranging from 154° to 225° and were readily soluble in organic solvents.

Drew (J., 1929, 560) has shown that during the evaporation, on the steam-bath, of an aqueous solution of dimethyltelluronium dihydroxide a mixed anhydride of trimethyltelluronium hydroxide and methyltellurinic acid is formed, from which trimethyltelluronium iodide and methyltelluronium tri-iodide are obtained on treatment with hydriodic acid. By the action of hydriodic acid on (II), (III), and (VI), ***di*-n-*butyltelluronium di-iodide*** and **n-*butyltelluronium tri-iodide*** are obtained, but tri-*n*-butyltelluronium iodide could not be identified amongst the products. It may therefore be inferred that migration of *n*-butyl radicals does not occur during the formation of the substances (II)—(VI). Mixtures of di-*n*-butyltelluronium di-iodide and *n*-butyltelluronium tri-iodide are also formed during the interaction of iodine with di-*n*-butyl telluride in carbon tetrachloride solution or with ethyl *n*-butyltelluroacetate in ethereal solution and by the interaction of hydriodic acid and di-*n*-butyltelluronium dihydroxide in acetone solution. The tri-iodide is also formed by the action of hydriodic acid in acetone solution on the di-iodide. The general reactions which lead to the formation of mixtures of the di- and tri-iodides are:

$$(1)\ \mathrm{TeR'I + RI \longleftarrow TeRR'I_2 \longrightarrow TeRI + R'I.}$$
$$(2)\ \mathrm{TeRI + I_2 \longrightarrow TeRI_3.}$$
$$(3)\ \mathrm{TeRI + RI \longrightarrow TeR_2I_2.}$$
$$(4)\ \mathrm{R{\cdot}TeO{\cdot}OH + 3HI \longrightarrow TeRI_3 + 3H_2O.}$$

Reactions of types (1), (2), and (4) have been observed by Edwards, Gaythwaite, Kenyon, and Phillips (*loc. cit.*) with *p*-tolylselenoacetic acid dibromide, *p*-bromoselenotoluene, and *p*-tolueneseleninic acid respectively, and of type (4) by Drew (*loc. cit.*) with methyltellurinic acid.

The l-*menthyl* ester of tellurodiacetic acid is obtained as a higher-boiling fraction in the thermal decomposition of the *l*-menthyl ester of di-*n*-butyltelluretine bromide. By oxidation of the *l*-menthyl ester in acetone solution with hydrogen peroxide, a compound, m. p. 90°, is obtained which is readily soluble in organic solvents, and is further distinguished from the products (I)—(VI) in that it oxidises hydriodic acid and rapidly decolorises aqueous potassium permanganate. The analysis of this substance agrees with that of a hydrated tellurone; it is therefore similar in properties and composition to the compound, described as a hydrated tellurone, which Morgan and Burgess (*loc. cit.*) obtained on oxidation of *cyclo*telluropentane. The results described above, however, suggest that tellurone formation would be preceded by extensive oxidation of the alkyl groups attached to the tellurium atom, and that products analogous to (I)—(VI), containing tellurinic acids, would be expected to be present in the oxidation products. The absence of such compounds suggests that the telluroxide, which is the primary product of the oxidation of *l*-menthyl tellurodiacetate, is stabilised by combination with hydrogen peroxide, forming a derivative analogous to the dihydroxide (VIII) and the hydroxy-nitrates (X), (XI). On this basis the compound obtained by oxidation of the *l*-menthyl ester is a *hydroxy-perhydrate* $(CH_2{\cdot}CO{\cdot}O{\cdot}C_{10}H_{19})_2\,Te(OH){\cdot}O{\cdot}OH$, and the compound which Morgan and Burgess described as a tellurone may be formulated in the same way as $C_5H_{10}{>}Te(OH){\cdot}O{\cdot}OH$. This suggestion is in agreement with the analyses of these two compounds and provides a better explanation of their oxidising action than does the assumption that tellurones are oxidising agents. The impure explosive dimethyltellurone (Found: C, 10·5; H, 3·2. Calc.: C, 12·7; H, 3·2%) described by Vernon (J., 1920, **117**, 889) was probably a similar compound (dimethyltelluroxyperhydrate, $C_2H_7O_3Te$, requires C, 11·2; H, 3·4%), mixed or in association with the complex $TeMe_2O,Me{\cdot}TeO_2H$ ($C_3H_{10}O_3Te_2$ requires C, 10·3; H, 2·9%).

EXPERIMENTAL.

Equivalent weights were determined by refluxing 0·1—0·3 g. of the substance in 0·05N-alcoholic potassium hydroxide and back titration with 0·1N-hydrochloric acid. The calculated values are g. of substance which would react with 56 g. of potassium hydroxide by neutralisation of acid groups and saponification of ester groups, in the formulæ proposed.

Di-n-*butyl Telluride*.—To a warmed solution of tellurium (40 g.), sodium formaldehyde-sulphoxylate ("rongalite," 90 g.), and sodium hydroxide (70 g.) in water (400 c.c.), *n*-butyl bromide (90 g.) in ethyl alcohol (350 c.c.) was slowly added with stirring, under reflux, a current of coal gas being passed through the apparatus. Di-*n*-butyl telluride (45 g.), isolated by extraction with ether, drying with calcium chloride, and removal of the ether, was stored under coal gas. After three redistillations it had b. p. 109—112°/12 mm., $d_{4^\circ}^{25^\circ}$ 1·2923, $n_D^{19^\circ}$ 1·5183. The telluride reacted with an equimolecular proportion of ω-bromoacetophenone, giving crystalline phenacyl-di-*n*-butyltelluronium bromide (XV), m. p. 87°, and with bromoacetic acid, giving a viscous uncrystallisable product.

Methyldi-n-*butyltelluronium Iodide* (XII).—A mixture of di-*n*-butyl telluride (12·1 g., 1 mol.) and methyl iodide (8·0 g., 1 mol.) became warm and rapidly set to a solid mass, which was washed with dry ether and recrystallised from chloroform. The product, *methyldi*-n-*butyltelluronium iodide* (16 g.), m. p. 159° (decomp.), was soluble in water (Found: C, 27·6; H, 5·0; I, 32·9; Te, 33·6. $C_9H_{21}ITe$ requires C, 28·2; H, 5·5; I, 33·1; Te, 33·3%).

l-*Menthyl Ester of Di*-n-*butyltelluretine Bromide* (XIV).—A mixture of *l*-menthyl bromoacetate (41·5 g., 1 mol.) and di-*n*-butyl telluride (36 g., 1 mol.) crystallised rapidly. After recrystallisation from ether–light petroleum, the *l*-menthyl ester of di-*n*-butyltelluretine bromide (62 g.) was obtained, m. p. 90°, $[\alpha]_{5461}^{17\cdot5^\circ}$ − 23·6° in chloroform (*l*, 2; *c*, 2·5), soluble in cold water, decomposed by hot water.

Ethyl Ester of Di-n-*butyltelluretine Bromide* (XIII).—A mixture of di-*n*-butyl telluride (24 g., 1 mol.) and ethyl bromoacetate (16·7 g., 1 mol.) crystallised rapidly. The solid was washed with light petroleum and recrystallised from chloroform–light petroleum. The *ethyl* ester of di-*n*-butyltelluretine bromide (35 g.), m. p. 62°, was soluble in ether and in water (Found: C, 35·2; H, 6·0; Te, 31·2. $C_{12}H_{25}O_2BrTe$ requires C, 35·3; H, 6·2; Te, 31·2%).

Ethyl n-*Butyltelluroacetate*.—The preceding ethyl ester (15 g.) decomposed on distillation under reduced pressure, the first fraction being *n*-butyl bromide and the second *ethyl* n-*butyltelluroacetate*, which after redistillation had b. p. 135—138°/21 mm., 85°/<0·1 mm., $n_D^{18^\circ}$ 1·5276 (Found: C, 36·3; H, 6·3; Te, 47·3. $C_8H_{16}O_2Te$ requires C, 35·4; H, 6·0; Te, 47·0%). The ester was stored under coal gas; yield, 8 g. The ester (4·2 g., 1 mol.) combined with ω-bromoacetophenone (3·0 g., 1 mol.) on gentle warming; from the product, by trituration with anhydrous ether and recrystallisation from chloroform–ethyl alcohol, the *ethyl* ester of phenacyl-*n*-butyltelluretine bromide (XVI) (0·3 g.) was obtained, m. p. 89°; it was soluble in acetone (Found: C, 40·5; H, 5·0; Te, 27·4. $C_{16}H_{23}O_3BrTe$ requires C, 40·8 H, 4·9; Te, 27·1%).

l-*Menthyl* n-*Butyltelluroacetate.*—The *l*-menthyl ester of di-*n*-butyltelluretine bromide (40 g.) decomposed at 100°/20 mm. with evolution of *n*-butyl bromide. The residue, distilled at < 0·1 mm., yielded l-*menthyl* n-*butyltelluroacetate* (18 g.), which after redistillation had b. p. 120—125°/0·1 mm., $[\alpha]_{5461}^{20^\circ}$ − 5·2° (*l*, 0·5), $d_4^{20^\circ}$ 1·2515, $n_D^{20^\circ}$ 1·5182 (Found: C, 50·2; H, 7·9; Te, 33·4. $C_{16}H_{30}O_2Te$ requires C, 50·3; H, 7·9; Te, 33·4%). The ester was stored under coal gas. The ester (12·4 g., 1 mol.) combined with ω-bromoacetophenone (6·5 g., 1 mol.) on gentle warming: the product was washed with anhydrous ether and recrystallised from chloroform–ethyl alcohol. The l-*menthyl* ester of phenacyl-*n*-butyltelluretine bromide (XVII) (12·3 g.) obtained had m. p. 106°, $[\alpha]_{5461}^{20^\circ}$ − 23·7° in chloroform (*l*, 2; *c*, 4·5), and was soluble in chloroform, insoluble in ethyl alcohol, acetone, and ether (Found: C, 49·2; H, 6·3; Te, 21·9. $C_{24}H_{37}O_3BrTe$ requires C, 49·6; H, 6·3; Te, 22·0%).

Ethyl and *l*-menthyl *n*-butyltelluroacetate each combined with an equimolecular proportion of methyl iodide; the products did not crystallise.

l-*Menthyl Tellurodiacetate.*—After removal of *l*-menthyl *n*-butyltelluroacetate from the decomposition products of the *l*-menthyl ester of di-*n*-butyltelluretine bromide (40 g.), the residue was dissolved in ether, and the solution filtered from deposited tellurium and concentrated. The yellow crystals which separated, recrystallised from methyl alcohol, yielded l-*menthyl tellurodiacetate* (11 g.), m. p. 58°, $[\alpha]_{5461}^{15^\circ}$ − 27·6° in ether (*l*, 2; *c*, 1·25), $[\alpha]_{5461}^{17\cdot5^\circ}$ − 34·4° in chloroform (*l*, 2; *c*, 1·25), soluble in all the common organic solvents (Found: C, 54·5; H, 7·9; Te, 25·4; equiv., 264. $C_{24}H_{42}O_4Te$ requires C, 55·3; H, 8·1; Te, 24·5%; equiv., 259).

Oxidation of Di-n-*butyl Telluride.*—(i) *By atmospheric oxygen.* The amorphous white *solid* (II) (3·2 g.) which was deposited from di-*n*-butyl telluride (25 g.) on exposure to air during 6 months decomposed at 180° and was very sparingly soluble in ethyl alcohol and in benzene (Found: C, 25·3; H, 5·3; Te, 55·8; equiv., 313. $C_{20}H_{48}O_7Te_4$ requires C, 26·4; H, 5·3; Te, 56·0%; equiv., 304).

(ii) *By hydrogen peroxide.* To a cooled solution of di-*n*-butyl telluride (5·8 g., 1 mol.) in acetone (15 c.c.), hydrogen peroxide (30%) was added until precipitation ceased. The white *solid* (VI) obtained (3 g.) was washed with water and dried in a vacuum. It decomposed at 180°, was sparingly soluble in acetone and in benzene, and readily soluble in hot ethyl alcohol, giving a solution which gelatinised on cooling (Found: C, 33·4; H, 6·3; Te, 52·1; equiv., 721. $C_{20}H_{46}O_4Te_3$ requires C, 32·8; H, 6·3; Te, 52·2%; equiv., 732). After removal of a second crop which separated (0·5 g.) (Found: C, 32·8; H, 6·4; Te, 52·0%), the mother-liquor was made alkaline, concentrated, acidified with sulphuric acid, and distilled (bath temp. 200°). The distillate, which had the smell of butyric acid, was neutralised (phenolphthalein) with aqueous calcium hydroxide and evaporated to dryness. The residue of calcium butyrate decomposed at 150° and was analysed by ignition with sulphuric acid (Found: Ca, 18·8. Calc. for $C_8H_4O_4Ca$: Ca, 18·7%).

(iii) *By alkaline hydrogen peroxide.* A solution of hydrogen peroxide (50 c.c. of 20%; 16 mols.) and potassium hydroxide (5 g., 4 mols.) in water (100 c.c.) was added slowly to di-*n*-butyl telluride (4·7 g., 1 mol.) in acetone (50 c.c.). The oil which separated solidified on cooling and was recrystallised from ethyl alcohol. The *di*-n-*butyltelluronium dihydroxide* (VIII) (3·5 g.) obtained, soluble only in acetone, lost water at 120° and the residue decomposed at 175° (Found: C, 34·5; H, 7·0; Te, 45·9. $C_8H_{20}O_2Te$ requires C, 34·9; H, 7·3; Te, 46·3%).

(iv) *By nitric acid.* The oil which separated when di-*n*-butyl telluride (5 g.) was refluxed with excess of dilute nitric acid solidified on cooling to a mass of colourless crystals of *di*-n-*butyltelluronium hydroxy-nitrate* (X) (5 g.), m. p. 84°, which was soluble in the common organic solvents, was decomposed to a white amorphous solid by water, and exploded at 120°/20 mm. (Found: C, 31·0; H, 5·7; Te, 40·1; equiv., 315. $C_8H_{19}O_4NTe$ requires C, 30·0; H, 6·0; Te, 39·8%; equiv., 320).

Oxidation of Ethyl n-*Butyltelluroacetate.*—(i) *By atmospheric oxygen.* The white *solid* (III) (1·2 g.) which separated from ethyl *n*-butyltelluroacetate (5 g.) on exposure to air during 2 months was washed with light petroleum and dried in a vacuum. It decomposed without melting at 180° and was soluble only in warm ethyl alcohol (Found : C, 25·3; H, 4·5; Te, 52·5; equiv., 250. $C_{16}H_{36}O_7Te_3$ requires C, 26·6; H, 5·0; Te, 53·0%; equiv., 241).

(ii) *By hydrogen peroxide.* Hydrogen peroxide (30%) was added to the ethyl ester, in acetone solution, until precipitation ceased. The amorphous white precipitate (III) had the same properties as that described in (i) (Found : C, 25·9; H, 5·2; Te, 53·7%; equiv., 245).

Oxidation of l-*Menthyl* n-*Butyltelluroacetate*.—(i) *By atmospheric oxygen.* n-*Butyltellurinic acid* (I) (1·4 g.) separated as a white solid from *l*-menthyl *n*-butyltelluroacetate (15 g.) on exposure to air during 8 months [Found : C, 22·8; H, 4·2; Te, 58·4; equiv. (determined as described on p. 344, but without refluxing), 217. $C_4H_{10}O_2Te$ requires C, 22·1; H, 4·6; Te, 58·6%; equiv., 213]. The acid decomposed at 250°, was sparingly soluble in warm ethyl alcohol, soluble with decomposition in carbon disulphide and in acetic acid, insoluble in cold 3N-aqueous potassium hydroxide, soluble in hot N-alcoholic potassium hydroxide, and decomposed by hot water, giving an alkaline solution (possibly of *n*-butyltelluronium trihydroxide) and an insoluble residue.

(ii) *With hyperol* (*urea perhydrate*). A solution of hyperol (0·4 g., 1 mol.) in ethyl alcohol (20 c.c.) was added to the *l*-menthyl ester (1·5 g., 1 mol.), with cooling. *n*-Butyltellurinic acid (0·25 g.), identical in properties with that described in (i) above, separated from the solution during 2 days (Found : C, 22·7; H, 4·3; Te, 58·2%; equiv., 216).

(iii) *By hydrogen peroxide.* Hydrogen peroxide (30%) was added to the *l*-menthyl ester (10 g.) in acetone solution (25 c.c.), until precipitation ceased. The *precipitate* (V) was separated, washed with water and with acetone, and dried in a vacuum (Found : C, 39·3; H, 6·4; Te, 41·8; equiv., 184. $C_{14}H_{40}O_5Te_2$ requires C, 39·1; H, 6·5; Te, 41·7%; equiv., 182). The substance decomposed at 220°, was soluble in chloroform, carbon disulphide, and pyridine, and slightly soluble in warm water, giving an alkaline solution. It lost weight (approx. 40%) on trituration with N-sodium carbonate; the alkaline extract contained tellurium but gave no precipitate on acidification, and the residue, which decomposed at 150°, was insoluble in all solvents.

The substance (V) (5 g.) on trituration with cold 3N-nitric acid was converted into a *substance* (VII), which decomposed with effervescence at 130°, was insoluble in organic solvents, but soluble in hot N-potassium hydroxide with liberation of menthol (Found : C, 36·5; H, 5·7; Te, 38·3; equiv., 210. $C_{20}H_{39}O_7NTe_2$ requires C, 36·4; H, 6·0; Te, 38·7%; equiv., 220). Trituration of (VII) with N-sodium carbonate left a residue insoluble in all solvents, the composition of which was not elucidated (Found : C, 33·0; H, 5·0; Te, 41·0%).

On addition of aqueous ammonia to the nitric acid washings separated in the preparation of (VII), an amorphous white precipitate (probably impure tellurium dioxide) was obtained (Found : C, 5·8; H, 1·0; Te, 77·7. Calc. for TeO_2 : Te, 79·9%. A second preparation gave C, 4·6; H, 1·4; Te, 74·6%).

(iv) *By nitric acid.* From a mixture of *l*-menthyl *n*-butyltelluroacetate (5 g., 1 mol.) and 6N-nitric acid (100 c.c., 5 mols.) the *hydroxy-nitrate* of *l*-menthyl *n*-butyltelluroacetate (XI) (6 g.) separated as a glassy solid. After being washed with water and dried in a vacuum, it had m. p. 42° (decomp. with efferv. at 140°) and was soluble in acetone, ethyl alcohol and ether, insoluble in other solvents and in water (Found : C, 42·5; H, 6·7; Te, 27·0; equiv., 223. $C_{15}H_{31}O_6NTe$ requires C, 41·7; H, 6·7; Te, 27·7%; equiv., 229). When heated at 100°/20 mm. for 1 hour, the hydroxy-nitrate lost weight (approx. 5%).

From a mixture of the hydroxy-nitrate (5 g., 1 mol.) and diethylamine (0·9 g., 1 mol.) in ether (50 c.c.) a white solid (3 g.) separated, which decomposed at 203° and was soluble in 6N-potassium hydroxide with liberation of menthol. On trituration of this product with water, diethylamine nitrate passed into solution; the insoluble *residue* (IV) decomposed at 210° (Found : C, 24·4; H, 4·6; Te, 55·1. $C_{14}H_{32}O_7Te_3$ requires C, 24·2; H, 4·6; Te, 55·1%).

From a mixture of equimolecular proportions of the hydroxy-nitrate and aniline in dry ether, aniline nitrate separated; a solid product could not be isolated from the filtered ethereal solution.

(v) *By benzoyl peroxide.* Benzoyl peroxide (2·4 g., 1 mol.) in chloroform (25 c.c.) was added to the *l*-menthyl ester (3·8 g., 1 mol.) in chloroform (25 c.c.). The mixture, which became warm, was heated under reflux for 1 hour, and the chloroform allowed to evaporate at room temperature. After 4 days, the deposited *dibenzoate of* *l*-menthyl *n*-butyltelluroacetate dihydroxide (IX) (5·4 g.) was removed, washed with water, and dried in a vacuum. It was soluble in ethyl alcohol, insoluble in water and in light petroleum (Found : C, 57·2; H, 6·7; Te, 19·8. $C_{30}H_{40}O_6Te$ requires C, 57·7; H, 6·5; Te, 20·4%).

Di-n-*butyltelluronium Di-iodide and* n-*Butyltelluronium Tri-iodide*.—(i) *From di*-n-*butyl* *telluride.* On evaporation at room temperature of a mixture of di-*n*-butyl telluride (2·4 g., 1 mol.) and iodine (2·6 g., 1 mol.) in carbon tetrachloride (50 c.c.), there was deposited a mixture of red crystals (3·5 g.), soluble in light petroleum, and a blue-black micro-crystalline powder, insoluble in light petroleum. The red crystals, recrystallised from light petroleum, gave *di-*n*-butyltelluronium di-iodide*, m. p. 61°, soluble in the common organic solvents, sparingly soluble in water (Found : C, 19·5; H, 3·6; I, 51·5; Te, 25·8; equiv., 245. $C_8H_{18}I_2Te$ requires C, 19·4; H, 3·6; I, 51·3; Te, 25·7%; equiv., 247). The blue-black powder was washed with light petroleum, leaving n-*butyltelluronium tri-iodide* (Found : C, 8·4; H, 1·9; I, 67·5; Te, 22·9. $C_4H_9I_3Te$ requires C, 8·5; H, 1·6; I, 67·3; Te, 22·6%), which was soluble in acetone and in ethyl alcohol and decomposed on heating, with liberation of iodine.

The di-iodide was recovered unchanged after trituration with hydriodic acid. On addition of hydriodic acid to the di-iodide in acetone solution, followed by evaporation of the acetone at room temperature, crystals of the tri-iodide were deposited.

(ii) *From di-*n*-butyltelluronium dihydroxide.* Hydriodic acid (10 c.c. of 50%; 2 mols.) was added slowly to the dihydroxide (2·8 g., 1 mol.), suspended in acetone (25 c.c.), and the resulting clear red solution was extracted with light petroleum. The extract, washed with water, dried (sodium sulphate), and concentrated at room temperature, deposited orange crystals of di-*n*-butyltelluronium di-iodide, m. p. 61°. The extracted solution, on evaporation, deposited *n*-butyltelluronium tri-iodide, which after recrystallisation from acetone was identical in properties with that described in (i) above.

(iii) *From* (II), (III), *and* (VI). Hydriodic acid (10 c.c. of 57%) was added to each of these compounds (3·2 g.), suspended in acetone (20 c.c.). The resulting di-iodide (Found : C, 19·9; H, 3·7; Te, 24·8%) and tri-iodide (Found : Te, 22·9%) were isolated as described in (ii) above.

(iv) *From ethyl* n-*butyltelluroacetate.* Iodine (2·5 g., 1 mol.) in ether (50 c.c.) was added slowly to the ethyl ester (2·7 g., 1 mol.) in ether (10 c.c.). The solution was evaporated at room temperature to 10 c.c. and extracted with light petroleum. The di-iodide, m. p. 60° (Found : C, 19·7; H, 3·8; Te, 25·1%), and tri-iodide (Found : C, 8·4 : H, 2·0; Te, 22·5%) were isolated as described in (i) above. The fluid by-products had the characteristic smell and lachrymatory effect of ethyl iodoacetate.

Oxidation of l-*Menthyl Tellurodiacetate.*—Addition of hydrogen peroxide (30%) to the *l*-menthyl ester in acetone solution precipitated a white solid, which was washed with water and with acetone and recrystallised from aqueous alcohol. The *hydroxy-perhydrate* of *l*-menthyl tellurodiacetate obtained had m. p. 90° (decomp. with efferv. at 145°) (Found : C, 50·9; H, 7·5; Te, 24·5. $C_{24}H_{44}O_7Te$ requires C, 50·5; H, 7·7; Te, 22·3%). It was soluble in ether, light petroleum, acetic acid, and alcohol, insoluble in water and in acetone. In acetic acid solution the hydroxy-perhydrate liberated iodine from potassium iodide and bromine from hydrobromic acid and rapidly decolorised aqueous potassium permanganate.

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