16. Further Experiments on the Oxidation of Alkyl Tellurides.

By Michael P. Balfe and Kamada N. Nandi.

Three amorphous insoluble oxidation products of high melting point have been obtained by the action of air or of hydrogen peroxide on di-*n*-amyl telluride and the ethyl and *l*-menthyl esters of *n*-amyltelluroacetic acid. They are n-*amyltellurinic acid*, $C_5H_{11}\cdot TeO\cdot OH$, a substance, $C_5H_{11}\cdot TeO\cdot CH_2\cdot CO_2Et,2C_5H_{11}\cdot TeO_2H$, and a *substance*, $3(C_5H_{11})_2TeO,C_5H_{11}\cdot TeO_2H$. Derivatives of quadrivalent tellurium obtained from the above three alkyl tellurides are freely soluble and of low melting point.

These observations are similar to those made by Balfe, Chaplin, and Phillips (J., 1938, 341) in experiments with other alkyl tellurides.

Balfe, Chaplin, and Phillips (J., 1938, 342), from an investigation on the oxidation of di-*n*-butyl telluride and other alkyl tellurides, suggested that the telluroxides which are the initial products of the oxidation are unstable and are rapidly converted into *n*-butyltellurinic acid, which is not a simple substance, but exists only as a complex polymeride. In some cases, telluroxide molecules may be incorporated in this polymeride and so become stabilised. This suggestion has not subsequently been controverted, and the properties of the substance described as the anhydride of methyltellurinic acid (Drew, J., 1929, 560), which, from the analytical figures given, may have been a similar complex, and the properties of certain substances described by Bird and Challenger (J., 1939, 163) are in harmony with it. The present experiments, on di-*n*-amyl telluride and certain of its derivatives, were undertaken to test and, if possible, to extend, the previous suggestions. The greater instability of the present compounds restricted the work and it can, therefore, only be said that the results obtained are in agreement with the suggestions made by Balfe, Chaplin, and Phillips (*loc. cit.*).

n-*Amyltellurinic acid* ($C_5H_{11}\cdot TeO\cdot OH$) was obtained by aerial oxidation of di-*n*-amyl telluride and the ethyl and *l*-menthyl esters of *n*-amyltelluroacetic acid ($C_5H_{11}\cdot Te\cdot CH_2\cdot CO_2H$).

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* Microanalyses by Dr. Strauss of Oxford.

The complex $3(C_5H_{11})_2TeO,C_5H_{11}{\cdot}TeO_2H$ was obtained by oxidation of the telluride with hydrogen peroxide; $C_5H_{11}{\cdot}TeO{\cdot}CH_2{\cdot}CO_2Et,2C_5H_{11}{\cdot}TeO{\cdot}OH$ was obtained by the action of hydrogen peroxide on ethyl *n*-amyltelluroacetate. The tellurinic acid and $C_5H_{11}{\cdot}TeO{\cdot}CH_2{\cdot}CO_2Et,2C_5H_{11}{\cdot}TeO{\cdot}OH$ decomposed without melting at 200° and were insoluble in water and in organic solvents. The substance $3(C_5H_{11})_2TeO,C_5H_{11}{\cdot}TeO_2H$ melted with decomposition at about 150° and was soluble only in alcohol and in chloroform. On the other hand, derivatives of quadrivalent tellurium were prepared which had true melting points and were soluble in a number of organic solvents. These observations are in good agreement with those made in the previous work.

Since it was previously suggested that the decomposition of the telluroxides involved the methylene group adjacent to the tellurium atom, the preparation of di-*tert*.-butyl telluride was attempted with the object of studying its oxidation products. The oil assumed to be the crude telluride rapidly decomposed, depositing tellurium. On treatment of the residual liquid with water, a brown solid separated. This contained a very high proportion of tellurium, and on heating suddenly evolved copious black fumes, leaving a residue of tellurium dioxide. Its properties, therefore, resembled those of ditelluromethane (Morgan and Drew, J., 1925, **127**, 533), but were not further examined, as the compound was unsuitable for the present investigation.

EXPERIMENTAL.

Di-*n*-amyl telluride, b. p. 138—140°/18 mm., 98—100°/2 mm., was obtained in 55% yield from amyl bromide by the method used by Balfe, Chaplin, and Phillips (*loc. cit.*) (Found : Te, 46·7. Calc. for $C_{10}H_{22}Te$: Te, 47·3%). The telluride reacted with an equimolecular proportion of (*a*) methyl iodide, giving methyldi-*n*-amyltelluronium iodide, m. p. 70° after recrystallisation from ether–light petroleum; (*b*) ethyl bromoacetate, giving the *ethyl* ester of di-*n*-amyltelluretine bromide, m. p. 50° after recrystallisation from hot light petroleum (Found : Te, 28·9; Br, 17·7. $C_{14}H_{29}O_2BrTe$ requires Te, 29·2; Br, 18·3%); (*c*) ω-bromoacetophenone, giving phenacyldi-*n*-amyltelluronium bromide, m. p. 84° after recrystallisation from aqueous acetone. These three telluronium compounds were freely soluble in organic solvents except ether and light petroleum.

Ethyl n-*amyltelluroacetate*, b. p. 140—150°/17 mm. (Found : Te, 45·6. $C_9H_{12}O_2Te$ requires Te, 44·7%), obtained by thermal decomposition of the ethyl ester of di-*n*-amyltelluretine bromide, reacted with benzoyl peroxide (1 mol.) in chloroform solution to give the corresponding *dibenzoate*, $C_5H_{11}{\cdot}Te(OBz)_2{\cdot}CH_2{\cdot}CO_2Et$, m. p. 77—78° after recrystallisation from aqueous alcohol (Found : C, 52·1; H, 5·4. $C_{23}H_{18}O_6Te$ requires C, 52·3; H, 5·4%). Attempts to isolate hydrolysis products after treatment of the dibenzoate with alkali were unsuccessful.

A dibenzoate was obtained in a similar way from *l*-methyl *n*-butyltelluroacetate by Balfe, Chaplin, and Phillips (*loc. cit.*); other examples of dibenzoate formation by reaction with benzoyl peroxide are from *cyclo*hexene (Gelissen and Merimans, *Ber.*, 1926, **59**, 666) and from triphenylbismuthine and triphenylstibine (Challenger and Wilson, J., 1927, 209).

Heat was generated when di-*n*-amyl telluride and *l*-menthyl bromoacetate were mixed in equimolecular proportion, but the pasty product could not be crystallised. On thermal decomposition it yielded *n*-amyl bromide and the *l*-menthyl ester of *n*-amyltelluroacetic acid (b. p. 78—85°/17 mm.).

Di-*n*-amyl telluride in acetone solution with equimolecular proportions of (*a*) mercuric chloride gave a precipitate containing two components which could not be separated (the precipitate was partly liquefied at 80°, and the residual solid liquefied at 135°), (*b*) mercuric iodide gave, after removal of acetone, a viscous product which could not be crystallised and on thermal decomposition regenerated the reactants, (*c*) mercuric bromide deposited crystals of the addition *compound*, m. p. 88° after recrystallisation from acetone (Found : C, 18·6; H, 3·3. $C_{10}H_{12}Br_2HgTe$ requires C, 19·0; H, 3·4%).

Crystalline substances could not be obtained from the viscous products formed by addition of iodine in chloroform or carbon tetrachloride solution to di-*n*-amyl telluride or ethyl *n*-amyltelluroacetate.

n-*Amyltellurinic Acid.*—The white solid which separated on exposure of di-*n*-amyl telluride or the ethyl or *l*-menthyl ester of *n*-amyltelluroacetic acid to air was insoluble in water and all organic solvents, soluble in aqueous sodium hydroxide, and reprecipitated by a slight excess of acid. After being washed with light petroleum, it decomposed between 200° and 220° (Found :

C, 26·4; H, 5·3; Te, 55·4; equiv., 222. $C_5H_{12}O_2Te$ requires C, 25·9; H, 5·2; Te, 55·5%; equiv., 231).

On addition of perhydrol (10 c.c.) to di-*n*-amyl telluride (10 g.) a white *solid* separated, which was soluble in alcohol or chloroform and insoluble in other solvents. After recrystallisation from chloroform–acetone (yield, 3·3 g.) it had m. p. 144° (decomp.) (Found : C, 38·2; H, 7·3; Te, 45·1. $C_{35}H_{78}O_5Te_4$ requires C, 38·6; H, 7·1; Te, 46·8%). A similar product, with a somewhat higher m. p. (152°, decomp.), was obtained when the reaction was carried out in acetone solution (Found : C, 38·6; H, 7·1%).

The white *solid* (4·5 g.) which separated when perhydrol (20 c.c.) was added to ethyl *n*-amyltelluroacetate (5 g.) was washed with hot alcohol and dried. It was insoluble in all solvents and in alkali, but soluble in dilute acid; it decomposed at 200° (Found : C, 29·2; H, 5·4; Te, 50·2. $C_{19}H_{42}O_7Te_3$ requires C, 29·8; H, 5·1; Te, 50·9%).

*Attempted Preparation of Di-*tert.*-butyl Telluride.*—The method described by Balfe, Chaplin, and Phillips (*loc. cit.*) was employed, using 34 g. of sodium hydroxide, 44 g. of " rongalite," 500 c.c. of water, 20 g. of tellurium, and 46 g. of *tert.*-butyl chloride in 200 c.c. of ethyl alcohol. The oil obtained from the dried ethereal extract was stored under coal gas. It rapidly deposited tellurium. On addition of water to the residual liquid, a brown solid separated, which gradually became black (Found : C, 16·0; H, 3·3; Te, 80·0%).

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BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, October* 30*th*, 1940.]