4. *Syntheses of 1 : 4-Telluroxan and Related Cyclic Tellurides.*

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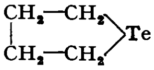
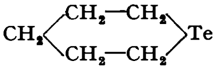
A simple synthesis of *cyclo*tellurobutane (I) and *cyclo*telluropentane (II) derivatives is described, and applied to the preparation of 1 : 4-*telluroxan* (III) and its derivatives. An account is also given of the reaction of tellurium and of sodium telluride with methylene, ethylene, and trimethylene dihalides.

VARIOUS cyclic tellurium compounds have been prepared in order to examine the possibility of their use as bactericidal or bacteriostatic agents (see Gulland and Farrar, *Nature*, 1944, **154**, 88), and these will be described in this and subsequent communications.

*cyclo*Tellurobutane (I) and *cyclo*telluropentane (II) (Morgan and Burgess, J., 1928, 321; Morgan and Burstall, J., 1931, 180) were synthesised by two methods: (1) the action of aluminium telluride (Al_2Te_3) on tetramethylene and pentamethylene dihalides between 125° and 175° gave mixtures of the cyclic telluridihalide with complex telluronium salts formed by secondary reactions; although the latter decomposed into the cyclic telluride when distilled in a vacuum, the syntheses are indirect and laborious and the yields were not good. (2) The reaction between tellurium and tetramethylene di-iodide at about 140° gave a good yield of *cyclo*telluributane di-iodide (Morgan and Burstall, *loc. cit.*), but this reaction was alleged by Morgan and Burgess (*loc. cit.*) to be almost a complete failure with pentamethylene dihalides. The present research has shown this to be incorrect; in fact, pentamethylene di-iodide and tellurium react to give the di-iodide of (II) in good yield.


(I.)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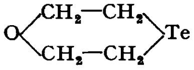
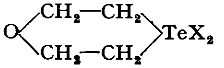

(III.)

A simpler and more satisfactory synthesis of these heterocyclic rings has, however, now been achieved by using sodium telluride, made *in situ* by the reaction of tellurium with a hot aqueous solution of sodium formaldehydesulphoxylate in an inert atmosphere (Tschugaev and Chlopin, *Ber.*, 1914, **47**, 1269). If the resulting solution is refluxed with an alkyl halide, the dialkyl telluride is formed (Balfe, Chaplin, and Phillips, J., 1938, 341; Challenger and Bird, J., 1939, 163; Balfe and Nandi, J., 1941, 70). As was expected, replacement of the alkyl halide by a 1 : 4- or 1 : 5-alkylene dihalide results in ring formation, and no difficulty was experienced in preparing pure *cyclo*telluributane dihalides from tetramethylene dibromide in yields of about 60% (based on tellurium used). Similarly, by using pentamethylene dichloride, *cyclo*telluripentane dihalides were produced, though in rather inferior yield (35%). This low yield is unlikely to be due to a greater reluctance to close a 6-membered than a 5-membered ring; it is probably to be traced to the fact that the slower reaction with the chloride encourages the formation of complex by-products, which was in fact observed. The melting points, solubilities, and general properties of these compounds agree very closely with those reported by Morgan and his co-workers (*locc. cit.*).

Since ββ′-dichlorodiethyl ether is now readily available, this method of ring-synthesis has been applied to the preparation of the hitherto unrecorded 1 : 4-*telluroxan* (III), and a series of its derivatives. 1 : 4-Telluroxan itself, prepared by reducing its dichloride with aqueous potassium metabisulphite, is a foul-smelling, yellow, low-melting solid, which is slowly oxidised in air but when pure is capable of being stored in a sealed tube without undergoing change. With halogens, telluroxan readily forms the stable crystalline *dihalides* (IV, X = halogen) and with methyl iodide gives the water-soluble *methiodide* (V).

When telluroxan dichloride is ground with excess of moist silver oxide, silver chloride is formed, together with a strongly alkaline solution of the *dihydroxide* (IV, X = OH), which can be obtained as a deliquescent, crystalline mass when the aqueous solution is evaporated to dryness under reduced pressure. It is a strong base; halogen acids regenerate the dihalides, and other acids yield a series of well-crystallised hydroxy-salts (VI, X = acid radical), of which the *hydroxy-nitrate*, *-picrate*, and *-picrolonate* were prepared. No indication was observed of the formation of hydroxy-halides.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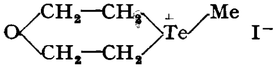
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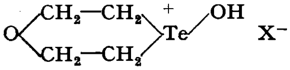
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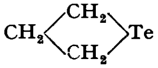
(VII.)

It was noted throughout the work on derivatives of 1 : 4-telluroxan that these are in general more polar in character than the corresponding *cyclo*telluri-pentane or -butane compounds. The dihalides, for example, are not soluble in non-polar solvents, but only in such solvents as alcohol (sparingly) and acetone; *cyclo*telluripentane dihalides, on the other hand, can be recrystallised from light petroleum, and the *cyclo*telluributane dihalides from benzene. The melting points of the telluroxan dihalides are much higher, and their order is Cl > Br > I, the reverse being the case for the other ring-systems. Further, no analogues of the crystalline hydroxy-salts have been recorded for the other cyclic tellurides.

The cause of these interesting differences between compounds of such very similar structure is obscure, but they are paralleled by the contrast between 1 : 4-selenoxan (Gibson and Johnson, J., 1931, 266) and *cyclo*selenopentane (Morgan and Burstall, J., 1929, 2197).

An attempt to make telluroxan di-iodide by the action of tellurium on ββ′-di-iododiethyl ether (Gibson and Johnson, J., 1930, 2526), following Morgan's second general method, was not very successful, probably owing to the instability of the ether, which breaks up on heating, giving iodine. The main product was a dark gum, from which the impure di-iodide could be isolated in 10—13% yield. The pure substance was most easily made by the neutralisation of aqueous telluroxan dihydroxide with hydriodic acid. In contrast to the two well-defined forms of the di-iodides of *cyclo*tellurobutane, *cyclo*telluropentane and *cyclo*telluropentanedione, telluroxan di-iodide appears to exist in only one form.

The study of the ring closure of αω-alkylene dihalides was completed by an investigation of trimethylene and ethylene derivatives.

Trimethylene dibromide reacted readily with aqueous sodium telluride even at room temperature, giving a nauseating substance which could be extracted with chloroform. The extract continually deposited a yellow gummy solid and combined with bromine, forming an ochre-coloured amorphous precipitate insoluble in all the usual solvents. Probably *cyclo*telluropropane (VII) is first formed, but, like the selenium analogue (Morgan and Burstall, J., 1930, 1497), readily polymerises to substances of high molecular weight; *cyclo*selenopropane is, however, sufficiently stable to be isolated. The polymeric dibromide reacted with moist silver oxide to give an alkaline solution, from which halogen acids precipitated gelatinous materials, and picric acid gave an amorphous picrate, soluble in glacial acetic acid, and melting at about 165° (decomp.).

Trimethylene di-iodide and tellurium at 120—150° yielded a black, apparently crystalline mass of very high m. p., almost entirely insoluble in all solvents; it contained some unchanged tellurium.

The reaction between ethylene dibromide and sodium telluride prepared by the Tschugaev–Chlopin method took a rather unexpected course. Neither cyclisation (to 1 : 4-ditelluran) nor polymer formation occurred, but even at room temperature tellurium was precipitated quantitatively and ethylene was liberated: $C_2H_4Br_2 + Na_2Te \longrightarrow C_2H_4 + 2NaBr + Te$.

When tellurium was heated in a sealed tube with ethylene dibromide at 160—170° for 16·5 hours, all but a minute amount was recovered unchanged.

Ethylene iodobromide (Simpson, *Proc. Roy. Soc.*, 1874, 51) was expected to react with tellurium according to the equation $2C_2H_4BrI + Te \longrightarrow (CH_2Br{\cdot}CH_2)_2TeI_2$, giving a substance offering many possibilities of ring-closure and having some possible physiological interest owing to its relationship with mustard gas. Even at 80°, however, ethylene was evolved, leaving a black substance of undetermined constitution; since this was readily hydrolysed by hot water to tellurium dioxide, it may have been tellurium di-iododibromide: $2C_2H_4BrI + Te \longrightarrow 2C_2H_4 + TeI_2Br_2$.

Attempts to prepare these ββ′-dihalogen diethyl telluride derivatives by the action of ethylene on tellurium tetrachloride or tetrabromide, in either carbon tetrachloride or hydrochloric (hydrobromic) acid, were equally unsuccessful, although syntheses of the selenium analogues by similar methods are known (Bausor, Gibson, and Pope, J., 1920, **117**, 1453; Bell and Gibson, J., 1925, **127**, 1877; Riley and Friend, J., 1932, 2342; Frick, *J. Amer. Chem. Soc.*, 1923, **45**, 1795; Heath and Semon, *J. Ind. Eng. Chem.*, 1920, **12**, 1100).

The reaction of tellurium with methylene iodide has been reported in a brief note by Drew (Newton Friend's " Textbook of Inorganic Chemistry," vol. XI, part IV, p. 186; otherwise unpublished) to give di-iodomethyl telluridi-iodide, $(CH_2I)_2TeI_2$, together with a red, amorphous polymer. Reduction of the di-iodide with aqueous metabisulphite is said to give di-iodomethyl telluride as a yellow crystalline substance polymerising above 75°, and as no other information was available, the reaction was re-investigated, since the telluride might, if obtainable in good yield, be of value for synthetic purposes.

It was soon found that the red polymer mentioned by Drew was always the main product. Consistent yields of di-iodomethyl telluridi-iodide were not obtained when amorphous tellurium was heated with methylene iodide (4—13 mols.) between 110° and 150°; the yield fluctuated irregularly with the conditions from 2% to 14%. The only moderately satisfactory result was obtained by heating tellurium (1 mol.) with methylene iodide (13 mols.) at 80° for 49 hours; the di-iodide was isolated in 30% yield, together with much red polymer. However, an exact repetition of the experiment gave only a 3·5% yield of di-iodide, and a much larger amount of polymer. The cause of these inconsistencies is not clear. The red polymer, which is unusually stable to potassium metabisulphite, has not been completely investigated and its constitution (cf. Drew, *loc. cit.*) remains obscure.

Reduction of the crystalline di-iodide with potassium metabisulphite gave di-iodomethyl telluride in quantitative yield. This substance, although apparently unimolecular (soluble in organic solvents, especially acetone) when freshly prepared, became polymerised and insoluble in acetone in the course of a few hours even at room temperature. It did not change in appearance, nor did its melting point alter; the latter fact is not surprising, since polymerisation is probably very rapid long before the melting point (180—185°) is reached, so that the m. p. of any specimen is that of the polymerised substance. When the freshly prepared monomer is dissolved in acetone, the solution, at first clear, quickly becomes turbid; evaporation of a few drops of the turbid solution on a slide showed a mixture of yellow fibrous needles (monomer) and irregular amorphous particles (polymer). Polymerisation probably takes place by telluronium salt formation between the bivalent tellurium atom and the two iodomethyl groups.

In view of the unsatisfactory properties of this telluride, no attempts were made to use it as an intermediate in the synthesis of ring compounds.

EXPERIMENTAL.

The tellurium micro-analyses were carried out by a new method soon to be published by Mr. J. E. Still.

cyclo*Telluributane Dibromide.*—Finely powdered, crystalline tellurium (2·0 g.), sodium formaldehydesulphoxylate (rongalite) (12 g.), and sodium hydroxide (8·5 g.) in water (75 c.c.) were refluxed in an all-glass apparatus consisting of a round-bottomed flask (500 c.c.) fitted with a reflux condenser, stirrer, and tube through which nitrogen was passed. When the original intense reddish-purple colour (polytelluride) had faded to a pale pink (30 minutes), the mixture was allowed to cool somewhat, and tetramethylene dibromide (4·5 g.; 1·3 mols.) added, and washed in with a little alcohol. Refluxing with vigorous stirring was then continued for 15 minutes; no sodium telluride was then left (as shown by a sample of the liquid remaining colourless on exposure to air). Rather dark-coloured drops of a foul-smelling oil were visible in the liquid; after cooling to room temperature, this was extracted thoroughly with chloroform, and the extracts dried over calcium chloride. A slight excess of bromine was added, and a small orange flocculent precipitate filtered off and rejected. On evaporation of the filtrate to small bulk, *cyclo*telluributane dibromide (3·8 g.; 70%) crystallised in 3 crops. This was twice recrystallised from benzene–light petroleum, giving pale yellow prisms (2·75 g.), m. p. 128—131° (Morgan and Burstall, *loc. cit.*, record m. p. 130°).

cyclo*Telluributane Dichloride.*—This was prepared in the same way, bromine being replaced by a stream of chlorine. The crude dichloride (yield, 71%) formed pure white crystals (2·35 g.), m. p. 112°—113° after recrystallisation from carbon tetrachloride (Morgan and Burstall record m. p. 111—112°).

cyclo*Telluripentane Dibromide.*—The sodium telluride solution was prepared as in the previous experiments; after it had been cooled to about 70°, pentamethylene dichloride (2·8 g.; 1·3 mols.) was added, and the mixture refluxed for 45 minutes. When cold, the oil was extracted with carbon tetrachloride, and the extracts dried over calcium chloride. Addition of a slight excess of bromine precipitated some sticky material. The liquor was decanted, evaporated to small bulk, and cleared from more suspended matter by shaking with norit and filtering. Crude dibromide (2·5 g.) was thrown down from the filtrate on addition of light petroleum; two recrystallisations from this solvent (b. p. 60—80°) gave colourless needles (1·85 g.; 33%), m. p. 106—107° (Morgan and Burgess, *loc. cit.*, record 105—107°).

*cyclo*Telluripentane dichloride was made similarly, chlorine being used instead of bromine. Here also gummy by-products were troublesome, and were removed with norit. The pure dichloride (1·55 g.; 37%) formed fluffy white needles, m. p. 105—106°, from light petroleum (b. p. 60—80°) (Morgan and Burgess report m. p. 106—107°).

cyclo*Telluripentane Di-iodide.*—Amorphous tellurium (1·0 g.) and pentamethylene di-iodide (5·05 g.; 2 mols.) were heated together in an oil-bath at 150° for 7 hours with frequent shaking. Excess of pentamethylene di-iodide was then removed by repeated shaking with light petroleum, and the residue taken up in hot acetone, leaving unchanged tellurium (0·06 g.). On evaporation, the acetone extracts gave the crude di-iodide (2·25 g.; 63%), which was very dark, melted at 115—117°, and appeared to contain excess of iodine, possibly as a periodide. After two recrystallisations from acetone (during which the lachrymatory odour of iodoacetone was observed), it formed orange-brown needles, m. p. 135—136·5° (Morgan and Burgess record m. p. 135—136° for both the forms obtained by them).

1 : 4-*Telluroxan* 1 : 1-*Dichloride* (IV, X = Cl).—A hot solution of sodium telluride was prepared from tellurium (6 g.), rongalite (36 g.), sodium hydroxide (25 g.), and water (210 c.c.); ββ′-dichlorodiethyl ether (8·0 g.; 1·5 mols.) in a little alcohol was added, and the mixture refluxed for 1 hour. After cooling to room temperature, the oil was extracted with chloroform, and the extracts dried over powdered calcium chloride. Chlorine was passed (external cooling) into the filtered chloroform solution until the discoloured gum first precipitated became a white, solid, semi-crystalline product. This was collected, mixed with the small crop obtained by evaporating the filtrate to small bulk, and extracted exhaustively with boiling acetone. The residue (*ca.* 4 g.) was a white, amorphous, insoluble substance which could not be crystallised, and was not further examined. On evaporation of the acetone solution, almost pure telluroxan dichloride was collected (5·9 g.; 46%). Two other similar experiments each gave 44·5% yields.

On two occasions, carbon tetrachloride was used instead of chloroform for extraction; in these cases the discoloured gum formed on chlorination did not alter on continued passage of chlorine, but on extraction with acetone the yield was very similar (40%, 47%), the insoluble residue being grey or black. A close search of the chloroform and acetone mother-liquors from these syntheses disclosed a further 3% of telluroxan dichloride but no other crystalline material.

Telluroxan dichloride crystallises from acetone in white plates, m. p. 179·5° (some decomp.) (Found: Cl, 26·2; Te, 46·6. $C_4H_8OCl_2Te$ requires Cl, 26·2; Te, 47·1%). It is moderately readily soluble in cold acetone, can be crystallised from boiling alcohol, but is very sparingly soluble in benzene, carbon tetrachloride and chloroform and insoluble in light petroleum. It is dissolved by boiling with water for some minutes, giving an acid solution which deposits a scanty amorphous white precipitate on cooling.

Telluroxan dibromide (IV, X = Br) was prepared in exactly the same way, bromine being substituted for chlorine. It separated from acetone in glittering platelets of a very pale yellow tinge, m. p. 157—158° (decomp.). Its properties and solubilities are similar to those of the dichloride (Found: Br, 43·5; Te, 35·4. $C_4H_8OBr_2Te$ requires Br, 44·5; Te, 35·5%).

Telluroxan Dihydroxide (IV, X = OH).—Telluroxan dichloride (2 g.) was ground in a glass mortar with a little water and silver oxide, prepared from silver nitrate (3 g.). After one hour the silver compounds were filtered off, and the filtrate evaporated to dryness under reduced pressure. The light grey residue was taken up in hot alcohol (10 c.c.), and the solution stirred with norit and filtered. The clear filtrate was evaporated in a vacuum desiccator, leaving the *dihydroxide* as a faintly discoloured, very deliquescent, waxy mass of radiating needles, freely soluble in water to give an alkaline solution (Found: Te, 53·3. $C_4H_{10}O_3Te$ requires Te, 54·6%). Accurate analytical figures were not obtained, owing to the hygroscopic nature of this substance.

The following four substances were prepared from the aqueous solution of the dihydroxide, made as described above.

Telluroxan Hydroxy-nitrate (VI, X = NO_3).—On the addition of a few drops of nitric acid a crop of heavy white crystals separated. After cooling to 0°, these were collected, and recrystallised from a small volume of water; yield, 0·4 g. from 1 g. of dichloride. The *hydroxy-nitrate* consists of short rods pointed at both ends, m. p. 190° (vigorous efferv.) (Found: N, 5·0; Te, 44·8. $C_4H_9O_5NTe$ requires N, 5·0; Te, 45·8%). It is rather soluble in water, and explodes feebly when heated in the free flame.

Telluroxan Hydroxy-picrate [VI, X = $C_6H_2(NO_2)_3{\cdot}O$].—Addition of hot aqueous picric acid solution formed a yellow precipitate, which was twice recrystallised from boiling water, giving radiating clusters of brilliant yellow needles, m. p. 238° (efferv.) after blackening above 210° (Found: N, 9·5, 9·5; Te, 28·6, 28·5. $C_{10}H_{11}O_9N_3Te$ requires N, 9·5; Te, 28·7%). Yield, 1·1 g. from 1 g. of the dichloride.

Telluroxan Hydroxy-picrolonate (VI, X = $C_{10}H_7O_5N_4$).—This was made in a similar manner, and recrystallised from a large bulk of hot water, in which it was rather sparingly soluble. It formed stellate clusters of thin rods, paler yellow than the picrate, m. p. 216° (violent efferv.) after darkening above 150° (Found: N, 11·5; Te, 26·5. $C_{14}H_{16}O_7N_4Te$ requires N, 11·7; Te, 26·6%).

Telluroxan Di-iodide (IV, X = I).—Neutralisation of the dihydroxide solution with dilute hydriodic acid gave a red crystalline precipitate of the *di-iodide*, which crystallised from acetone in large, bright red prisms, m. p. 155° (decomp.) (Found: Te, 28·0. $C_4H_8OI_2Te$ requires Te, 28·1%). In solvents other than acetone it is rather sparingly soluble.

Other Reactions of Telluroxan Dihydroxide Solution.—Hydrochloric and hydrobromic acids gave immediate crystalline precipitates of the dihalide. Sulphuric, hydrofluoric, acetic, formic, oxalic, perchloric and chromic acids gave no precipitates; the perchlorate was isolated as a mass of white needles by evaporation on the steam-bath, but it was very hygroscopic and analytical results were poor.

1 : 4-*Telluroxan* (III).—Telluroxan dichloride (10 g.), potassium metabisulphite (17 g.), water (100 c.c.), and carbon tetrachloride (50 c.c.) were shaken together in a separating funnel until all but a trace of solid had disappeared. The carbon tetrachloride layer was removed, the aqueous layer extracted twice more, and the mixed extracts dried over calcium chloride. It was then necessary to leave the solution overnight, during which time a brown, varnish-like film was deposited on the walls of the flask. Most of the solvent was next removed on the water-bath, considerable deposition of amorphous polymer occurring during the process. The residue was distilled under reduced pressure in an all-glass apparatus, nitrogen being passed through the capillary. After removal of residual solvent, telluroxan (*ca.* 6 g.) passed over as a lemon-yellow oil, b. p. 90°/21 mm., with a nauseating and moderately persistent odour. Owing to this unpleasant property, not as many experiments were made as would otherwise have seemed desirable. When supercooled at 0° to $-5°$, telluroxan crystallised and then had m. p. 6°; the initial solidification necessitated cooling to $-40°$. It had $n^{18°}$ 1·6340 for white light and $d^{20°}$ 1·8, and was miscible with the usual organic solvents but insoluble in water (Found: C, 24·0; H, 4·3; Te, 63·8. C_4H_8OTe requires C, 24·0; H, 4·0; Te, 63·9%). Although the solution of crude telluroxan in carbon tetrachloride seemed so unstable, the pure liquid showed no particular tendency to change, and could be kept for at least 18 months in sealed tubes in the dark. As expected, it gave immediate precipitates of dihalides when treated with bromine in carbon tetrachloride or iodine in alcohol. When a few drops were left exposed to the air for 36 hours, the liquid partly evaporated and was partly converted into the sticky crystalline dihydroxide.

Telluroxan Methiodide (V).—On addition of excess of methyl iodide to an acetone solution of telluroxan, the *methiodide* soon began to separate; it was recrystallised by suspending it in boiling alcohol, adding water until it dissolved, stirring in a little norit, filtering and cooling. It formed extremely pale yellow needles, m. p. 199° (efferv.), after becoming brown above 120°; it was easily soluble in water, sparingly in alcohol and acetone (Found: C, 17·7; H, 3·5; Te, 37·1. $C_5H_{11}OITe$ requires C, 17·6; H, 3·2; Te, 37·4%).

Di-iodomethyl Telluridi-iodide.—Only the most successful preparation is described. Amorphous tellurium (1 g.) and methylene iodide (26 g.) were heated at 80° for 49 hours. The excess of methylene iodide was removed under reduced pressure, and the residue extracted exhaustively with boiling alcohol. The alcoholic liquors yielded crude di-iodide (1·55 g.; 30%); the residue (1·5 g.) was a mixture of tellurium and red polymer. *Di-iodomethyl telluridi-iodide* crystallised from alcohol or acetone in dark red, irregular crystals, m. p. 127°, very sparingly soluble in other solvents (Found: C, 3·6; H, 0·7; Te, 19·5. $C_2H_4I_4Te$ requires C, 3·6; H, 0·6; Te, 19·2%).

Di-iodomethyl Telluride.—The di-iodide (1·12 g.) was ground for 20 minutes with potassium metabisulphite (1·1 g.; 3 mols.) and a little water. The yellow solid was collected and dried in a vacuum desiccator; yield, 0·69 g. (quantitative). On heating, it became orange above *ca.* 80°, softened about 155°, and melted with blackening and intumescence at 180—185° (Found: Te, 31·2. $C_2H_4I_2Te$ requires Te, 31·2%).

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