XXIV.—cyclo*Tellurobutane* (*Tetrahydrotellurophen*).

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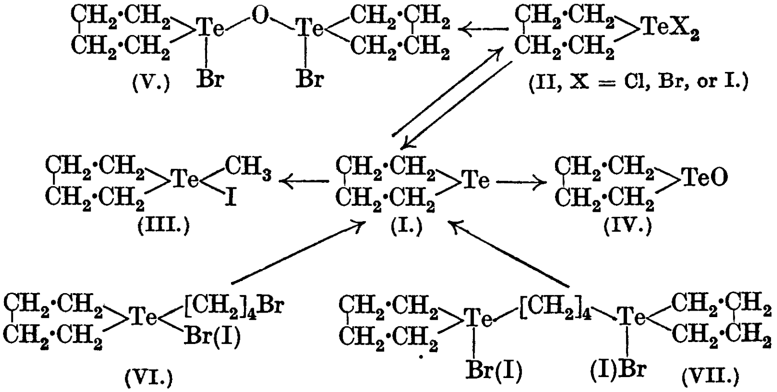
The earliest known saturated cyclic tellurohydrocarbon, namely, *cyclo*telluropentane, was first prepared by a method involving condensation between αε-pentamethylene dihalides and aluminium telluride (Morgan and Burgess, E.P. 292222; J., 1928, 322), a process which has now been employed in producing the five-membered homologue (I). But in the course of our investigation a more direct method has been devised whereby tellurium is combined additively with alkylene dihalides, and this process, which is of general application, has the technical advantage of obviating a preliminary preparation of readily decomposable metallic tellurides.

Amorphous tellurium dissolves in αδ-tetramethylene di-iodide at 130° with quantitative production of cyclo*telluributane* 1 : 1-*di-iodide* (II), $I[CH_2]_4I + Te = C_4H_8{:}TeI_2$, and this additive compound can be reduced to cyclo*tellurobutane* or *tetrahydrotellurophen* (I), a pale yellow oil of repulsive odour which oxidises rapidly in air to cyclo*telluributane* 1-*oxide* (IV). The cyclic tellurohydrocarbon also furnishes very stable *cyclo*telluributane 1 : 1-dihalides (II), which remain unchanged at temperatures considerably above their melting points, and moreover the *dichloride* and *dibromide* dissolve in hot water to acid solutions, from which they crystallise unchanged on cooling. *cyclo*Telluributane 1 : 1-dibromide gives a well-defined *bis*cyclo*telluributane* 1 : 1′-*oxydibromide* (V) when treated with one equivalent of alkali or when mixed with a molecular proportion of *cyclo*telluributane 1-oxide. Mercuric chloride and methyl iodide give with the tellurohydrocarbon the characteristic cyclo*telluro-butane mercurichloride* and *methiodide* (III).



When tetramethylene dibromide and aluminium telluride are heated together, a vigorous reaction commences at 125° and the water-soluble telluronium salts, 1-*bromobutyl*cyclo*telluributane* 1-*bromide* (VI) and *tetramethylene*-αδ-*bis*cyclo*telluributane* 1 : 1′-*di-bromide* (VII) are formed; but the presence of *cyclo*telluributane 1 : 1-dibromide was not detected (compare Morgan and Burgess, *loc. cit.*). The two foregoing telluronium bromides dissociate on heating into tetramethylene dibromide and *cyclo*tellurobutane, whereas when their aqueous solutions are treated with potassium iodide, 1-*bromobutyl*cyclo*telluributane* 1-*iodide* (VI) and *tetramethyl-ene*-αδ-*bis*cyclo*telluributane* 1 : 1′-*di-iodide* (VII) are formed respectively.

In their physical and chemical properties the foregoing telluronium salts derived from *cyclo*tellurobutane resemble closely those from *cyclo*telluropentane (*loc. cit.*). A similar resemblance exists between the dihalides of the two cyclic tellurohydrocarbons. One difference, however, is noteworthy : *cyclo*telluripentane di-iodide was obtained in two well-defined forms, an orange-yellow modification crystallising from hot solutions and passing at the ordinary temperature into deep red prisms with purple-blue reflex (Morgan and Burgess, *loc. cit.*; Gilbert and Lowry, J., 1928, 2658). *cyclo*Telluributane di-iodide crystallises from acetone in purple plates, whereas from hot benzene it separates in red crystals. There is far less contrast between these two modifications and both remain unchanged at the ordinary temperature.

EXPERIMENTAL.

cyclo*Tellurobutane* (*Tetrahydrotellurophen*) (I).—αδ-Tetramethylene glycol was prepared by reduction of diethyl succinate with sodium and dry alcohol and converted into the corresponding dibromide by the action of hydrogen bromide (compare Müller, *Monatsh.*, 1928, **49**, 27). αδ-Tetramethylene di-iodide was obtained by refluxing the foregoing dibromide with excess of a 15% acetone solution of sodium iodide. After removal of sodium bromide and excess of the solvent the residue of di-iodide was rectified under reduced pressure, b. p. 177°/178 mm.

Amorphous tellurium (10 g.) was heated at 130—140° with αδ-tetramethylene di-iodide (63 g.) for 5 hours with occasional shaking. The dark solution was filtered hot from undissolved tellurium and, on cooling, most of the product crystallised. A further quantity of di-iodide was obtained by precipitation with petroleum (b. p. 40—60°), from which αδ-tetramethylene di-iodide (38 g.) was recovered. *cyclo*Telluributane 1 : 1-di-iodide (*vide infra*), purified by crystallisation from acetone, was reduced by passing sulphur dioxide into its boiling aqueous suspension. The tellurohydrocarbon volatilised in steam and was collected under cold water. The heavy reddish-yellow oil was extracted with chloroform, dried over calcium chloride, and rectified in carbon dioxide under reduced pressure, b. p. 105—106°/122 mm.; 166—167°/761 mm. (Siwoloboff method); $n_D^{18^\circ}$ 1·6175 (Found: C, 25·9; H, 4·2; Te, 69·3. C_4H_8Te requires C, 26·15; H, 4·4; Te, 69·45%). This tellurohydrocarbon, which possessed a very penetrating and unpleasant odour, was miscible in all proportions with organic solvents but was insoluble in water. cyclo*Tellurobutane* oxidised readily in air, reacted explosively with concentrated nitric acid, and developed a red coloration with sulphuric acid.

cyclo*Tellurobutane mercurichloride*, $C_4H_8{:}Te,HgCl_2$, separated in white crystals when alcoholic solutions of its generators were mixed. After recrystallisation it melted at 146—147° with sintering at 140°. The characteristic odour of *cyclo*tellurobutane was observed when the mercurichloride was warmed with aqueous caustic soda (Found: Cl, 15·6. $C_4H_8Cl_2TeHg$ requires Cl, 15·6%).

cyclo*Telluributane* 1 : 1-*dichloride* (II) crystallised in white needles when chlorine was passed into a solution of the cyclic telluride or when concentrated hydrochloric acid was added to a solution of *cyclo*telluributane oxide (*vide infra*); m. p. 111—112° (Found: Cl, 27·8. $C_4H_8Cl_2Te$ requires Cl, 27·9%). It dissolved in warm water, crystallised unchanged on cooling, and was stable to above 200°; moreover it dissolved in the common organic solvents.

cyclo*Telluributane* 1 : 1-*dibromide* (II), obtained in yellowish-white prisms when solutions of its generators were mixed, was crystallised from benzene (Found: C, 13·8; H, 2·2; Br, 46·7. $C_4H_8Br_2Te$ requires C, 14·0; H, 2·3; Br, 46·5%). After melting to a clear liquid at 130°, it remained unchanged to 210°; a yellow colour then developed and bubbles of gas appeared. The dibromide was soluble in most organic media, dissolved sparingly in hot water to an acid solution, and crystallised unchanged on cooling.

cyclo*Telluributane* 1 : 1-*di-iodide* (II), obtained by heating tellurium with excess of tetramethylene di-iodide (*vide supra*) or by adding iodine to a solution of *cyclo*tellurobutane, crystallised from acetone in shining purple plates, whereas hot benzene solutions gave the di-iodide in bright red, prismatic crystals. Both these forms melted without decomposition at 149—150° and remained unchanged above 200°. The red crystals darkened above 100°, but under normal conditions both forms remain unchanged. The di-iodide was not appreciably soluble in water and only sparingly soluble in alcohol, but it dissolved in the common organic solvents (Found: I, 58·2; Te, 28·9. $C_4H_8I_2Te$ requires I, 58·0; Te, 29·15%).

*Bis*cyclo*telluributane* 1 : 1′-*oxydibromide* (V) was formed when *cyclo*telluributane 1 : 1-dibromide and oxide were warmed in equimolecular proportion in aqueous solution or by the addition of sufficient sodium carbonate or sodium hydroxide to remove half the bromine from the telluridibromide. The sparingly soluble oxybromide separated from warm water in small white prisms, m. p. 207° (decomp.) (Found: C, 17·7; H, 3·1; Br, 29·5. $C_8H_{16}OBr_2Te_2$ requires C, 17·7; H, 3·0; Br, 29·45%). Caustic alkalis converted it into the telluroxide (IV), whereas hydrobromic acid regenerated the dibromide (II).

cyclo*Telluributane* 1-*oxide* (IV), arising from the aerial oxidation of *cyclo*tellurobutane, also resulted from the action of caustic or carbonated alkalis on *cyclo*telluributane 1 : 1-dihalides. This white microcrystalline product melted at 241° (decomp.) (Found: Te, 63·25. C_4H_8OTe requires Te, 63·9%). It was soluble in water, alcohol, or acetone; halogen acids regenerated the corresponding dihalides.

cyclo*Telluributane* 1-*Methiodide* (III).—*cyclo*Tellurobutane and methyl iodide combined at once with generation of heat; the colourless product crystallised from water in needles (Found: I, 38·8. $C_5H_{11}ITe$ requires I, 39·0%). Although soluble in water or alcohol, the *methiodide* was insoluble in other common organic media. It darkened at 200° and vaporised rapidly without melting at 240°.

Aluminium Telluride and αδ-Tetramethylene Dibromide.—Aluminium telluride (30 g.) and tetramethylene dibromide (67 g.) were heated in a flask fitted with a ground-glass air condenser; a vigorous reaction commenced at 125°. The mixture was removed from the source of heat and shaken while the reaction was moderated by cooling if necessary. A little hydrogen bromide was evolved and the heating was continued at 125° for 2 hours; the cooled semi-solid mixture was then extracted successively with carbon tetrachloride, acetone, alcohol, and water. Tetramethylene dibromide (10 g.) was recovered from the carbon tetrachloride extract and a black insoluble residue (12 g.) remained.

1-δ-*Bromobutyl*cyclo*telluributane* 1-*bromide* (VI), obtained from the acetone and alcoholic extracts of the foregoing reaction product, crystallised from alcohol in white shining threads (Found: C, 23·7; H, 4·15; Br, 39·6. $C_8H_{16}Br_2Te$ requires C, 24·0; H, 4·0; Br, 40·0%). This complex bromide was soluble in water but did not dissolve in benzene or chloroform. When heated, it melted at 152—153° and dissociated above its melting point into tetramethylene dibromide and *cyclo*tellurobutane. Aqueous potassium iodide and this telluronium bromide gave a yellow microcrystalline precipitate of 1-δ-*bromobutyl*cyclo*telluributane* 1-*iodide*, which melted at 175—176° (decomp.) after recrystallisation from alcohol (Found: C, 21·4; H, 3·7. $C_8H_{16}BrITe$ requires C, 21·5; H, 3·6%).

Tetramethylene-αδ-*bis*cyclo*telluributane* 1 : 1′-*dibromide* (VII) crystallised from an aqueous extract of the interaction of aluminium telluride and tetramethylene dibromide. The white microcrystalline salt contained one molecule of water of crystallisation (Found: C, 23·5; H, 4·5; Br, 26·7; loss at 110°, 2·8. $C_{12}H_{24}Br_2Te_2,H_2O$ requires C, 23·3; H, 4·4; Br, 26·6; H_2O, 3·0%). This complex dibromide melted at 225° with dissociation into tetramethylene dibromide and *cyclo*tellurobutane. With aqueous solutions of the dibromide, silver nitrate gave a precipitate of silver bromide, whereas platinic chloride furnished a small quantity of a red chloroplatinate, m. p. 135° (decomp.).

Tetramethylene-αδ-*bis*cyclo*telluributane* 1 : 1′-*di-iodide* (VII), precipitated from aqueous solution of the foregoing dibromide on the addition of potassium iodide, redissolved to a colourless solution in water but separated therefrom in deep yellow, sparingly soluble crystals which decomposed at 215° (Found: I, 37·3. $C_{12}H_{24}I_2Te_2$ requires I, 37·5%).

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