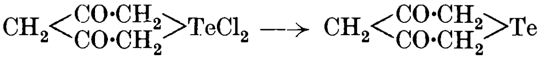
XLIV.—cyclo*Telluropentane.*

By GILBERT T. MORGAN and HENRY BURGESS.

AN investigation of the interactions of tellurium tetrachloride and acetylacetone by one of us (G. T. M.) and H. D. K. Drew led in 1921 to the discovery of *cyclo*telluripentane-3 : 5-dione 1 : 1-dichloride (I) and *cyclo*telluropentane-3 : 5-dione (II), these substances being the simplest members of two new series of organometalloidal compounds in both of which tellurium is implicated in a six-membered ring (J., 1920, **117**, 1456; 1923, **123**, 444; 1924, **125**, 731, 1601; *J. Soc. Chem. Ind.*, 1924, **43**, 40, 304).

(I.)  (II.)

$$CH_2\left<\begin{matrix}CO\cdot CH_2\\ CO\cdot CH_2\end{matrix}\right>TeCl_2 \longrightarrow CH_2\left<\begin{matrix}CO\cdot CH_2\\ CO\cdot CH_2\end{matrix}\right>Te$$

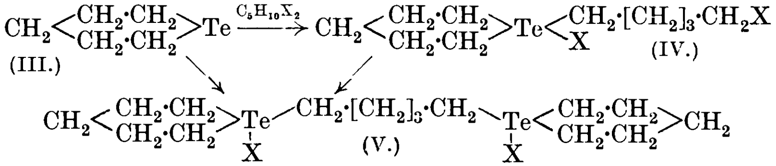
The series containing bivalent tellurium are yellow compounds sparingly soluble in cold water, and in collaboration with E. A. Cooper it was found that these aqueous solutions had considerable bactericidal potency in broth media (Morgan, Drew, and Cooper, J., 1922, **121**, 923; *Biochem. J.*, 1923, **17**, 30), whereas this intense germicidal action diminished very considerably when the compounds were employed in serum (*Biochem. J.*, 1924, **18**, 190).

On account of the noteworthy chemical and bacteriological properties of the new cyclic tellurium derivatives, it became desirable to obtain if possible the non-oxygenated *cyclo*telluropentane (III), which may be regarded as the parent tellurohydrocarbon of the two series (I and II).

Attempts made to prepare the dibromide or di-iodide of *cyclo*telluropentane by heating tellurium with αε-pentamethylene dibromide or di-iodide gave only small yields of cyclic products even when the amorphous metalloid was prepared, whereas the dichloride did not interact with tellurium under these conditions. A satisfactory preparation was achieved, however, by condensing a metallic telluride, preferably the aluminium compound, with a αε-pentamethylene dihalide; the *cyclo*telluropentane ring was then produced in accordance with the following equation, which represents this interaction with the dibromide :

$$Al_2Te_3 + 3CH_2Br\cdot[CH_2]_3\cdot CH_2Br = 3C_5H_{10}\colon Te + 2AlBr_3$$

The tellurohydrocarbon is not, however, isolated at this stage, since it combines additively with more of the alkylene dihalide to form two complex telluronium bromides. The following diagram illustrates the general course of the condensation when X = Cl,Br, or I :



$$CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>Te \xrightarrow{C_5H_{10}X_2} CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>Te<\genfrac{}{}{0pt}{}{CH_2\cdot[CH_2]_3\cdot CH_2X}{X}$$

(III.) (IV.)

$$CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>\underset{X}{Te}\diagup CH_2\cdot[CH_2]_3\cdot CH_2\diagdown\underset{X}{Te}<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>CH_2$$

(V.)

1-ε-*Bromoamyl*cyclo*telluripentane* 1-*bromide* (IV) and *pentamethylene-αε-bis*cyclo*telluripentane* 1 : 1′-*dibromide* (V) both dissolve in water, the latter being the more soluble.

In addition to these complex bromides a small amount of cyclo*telluripentane* 1 : 1-*dibromide*, $CH_2<\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}>TeX_2$ (VI), is produced during the condensation, probably through the interaction of moisture unavoidably introduced during the reaction; the unstable hydrogen telluride thereby set free readily furnishes amorphous tellurium, which interacts with pentamethylene dibromide. This dibromide (VI) is, however, more readily prepared by adding the calculated amount of bromine to the mixture of *cyclo*telluropentane and αε-pentamethylene dibromide produced by the thermal dissociation of the foregoing two complex telluronium bromides when these salts are heated under reduced pressure.

The condensation with aluminium telluride and αε-pentamethylene dichloride takes a similar course, except that no *cyclo*telluripentane dichloride is formed and a little *cyclo*telluropentane is detected by its odour and by the presence of its solid oxidation product (*cyclo*telluripentane oxide).

The complex telluronium salts, 1-ε-*chloroamyl*cyclo*telluripentane* 1-*chloride* (IV) and *pentamethylene-αε-bis*cyclo*telluripentane* 1 : 1′-*dichloride* (V), resemble the corresponding bromides, but are more readily soluble in water and the alcohols. cyclo*Telluripentane* 1 : 1-*dichloride* (VI) is prepared by adding chlorine to the foregoing complex chlorides or to the products of their thermal dissociation. cyclo*Telluropentane* (III), prepared by the reduction of *cyclo*telluripentane 1 : 1-dibromide with aqueous alkali metabisulphite (Morgan and Drew, *loc. cit.*), is so readily oxidised in air that it must be distilled in an inert atmosphere, being thus obtained as a light yellow oil which assumes a reddish-orange tint on exposure to light even in a sealed tube. It is more stable towards reducing agents than are the *cyclo*telluropentane-3 : 5-diones, since there is very little tellurium eliminated during the reduction of the dibromide with bisulphite.

The condensation between aluminium telluride and the αε-pentamethylene dihalides follows a well-marked gradation, the di-iodide reaction taking place most readily, whereas the dichloride reaction requires the highest temperature.

The tendency to form the simple *cyclo*telluripentane dihalides (VI) increases with the atomic weight of the halogen. A similar gradation of properties was observed in regard to recombination of the products of the thermal dissociation of the three 1-ε-halogenoamyl*cyclo*telluripentane 1-halides. The chloro-compound (IV) when melted in a sealed tube shows no disposition to resolidify on further heating, whereas in these circumstances both the bromo- and the iodo-derivative resolidify.

*cyclo*Telluripentane 1 : 1-di-iodide (VI), produced by direct addition of iodine to *cyclo*telluropentane in carbon tetrachloride, exists in two differently coloured forms : (α) a deep red modification with a purple-blue reflex, this variety being stable at the ordinary temperature in the presence of light, and (β) an orange modification which separates from hot solvents and passes slowly into the deep red form at the ordinary temperature, especially when exposed to light. The deep red modification crystallises from cold solutions, although occasionally it is accompanied by crystals of the orange form.

Bactericidal Action of cyclo*Telluropentane Derivatives.*

For the following preliminary bacteriological data we are indebted to Dr. H. Barnes.

The complex bromides (IV and V) have only slight bactericidal action, whereas *cyclo*telluropentane and *cyclo*telluripentane 1 : 1-dibromide and dichloride (VI) are considerably more potent and give approximately the same bactericidal coefficient with *Bacillus coli*, a result which indicates that in these cases the active agent is *cyclo*telluripentane 1 : 1-dihydroxide, produced either by hydrolysis of the dihalides or by wet oxidation of *cyclo*telluropentane. This bactericidal value is considerably less than the coefficients obtained with the *cyclo*telluropentane-3 : 5-dione series, but, unlike the latter, it is far less affected in serum, a result which is sufficiently promising to merit further investigation.

EXPERIMENTAL.

Although tellurium has been shown to combine with methyl iodide to form dimethyltelluronium di-iodide (Demarçay, *Bull. Soc. chim.*, 1883, **40**, 99; Scott, P., 1904, **20**, 157; Vernon, J., 1920, **117**, 86, 889), yet the corresponding reaction with pentamethylene di-iodide only occurred to a slight extent. When either pentamethylene di-iodide or dibromide was heated in xylene with amorphous tellurium for 20 hours, a 10% yield of the corresponding *cyclo*telluripentane dihalide was obtained and about 80% of the tellurium was recovered unchanged. The powdered metalloid seemed to be quite as effective in the case of the polymethylene di-iodide, but no cyclic compound was formed with the dibromide under various conditions. Owing to the small yield in these experiments recourse was had to the condensation taking place between the αε-pentamethylene dihalides and metallic tellurides (Morgan and Burgess, E. P. 7030 of 1927).

Pentamethylene di-iodide was prepared by refluxing the corresponding dibromide with a 15% solution of anhydrous sodium iodide in dry acetone for 1 hour. The sodium bromide was filtered off and the liquid fractionated in a vacuum (yield, 90% of the theoretical).

Aluminium telluride (27 g.) and pentamethylene dibromide (63·5 g.) were heated under reflux until at 165° (approximately) a reaction ensued which caused the dibromide to boil vigorously. This ebullition was moderated by cooling and stirring, and the heating was subsequently continued for 1 hour. The semi-solid product was then extracted successively with (*a*) carbon tetrachloride to remove unchanged pentamethylene dibromide and most of the *cyclo*telluripentane 1 : 1-dibromide; (*b*) moist acetone to dissolve the remaining *cyclo*telluripentane 1 : 1-dibromide, and 1-ε-bromoamyl*cyclo*telluripentane 1-bromide, this solvent also extracting some of the pentamethylene-αε-bis*cyclo*telluripentane 1 : 1′-dibromide and aluminium bromide; (*c*) water or moist methyl alcohol to extract the remainder of the aluminium bromide and bis*cyclo*telluri-compound from a dark grey, insoluble residue (6·7 g.). By fractional crystallisation of the three extracts the following yields of organic tellurium derivatives were obtained: (IV), 14 g.; (V), 23 g.; (VI), 2 g. The proportion of (VI) was always small, but the relative amounts of (IV) and (V) were variable, the yield of (IV) being diminished on decreasing the proportion of pentamethylene dibromide. If, however, the quantity of this reagent was diminished by one-third, the amount of insoluble residue was increased considerably. When magnesium telluride was employed in the condensation, the reaction commenced only at 200° (approximately) and the yield of soluble organo-tellurium derivatives was comparatively small.

Condensations with $\alpha\varepsilon$-pentamethylene dichloride and aluminium telluride were less vigorous, a higher temperature (175—185°) being required to start the reaction. Two tellurichlorides only were obtained (corresponding with IV and V), but the presence of *cyclo*telluripentane 1 : 1-dichloride was not detected, although the carbon tetrachloride extract indicated by its odour, colour, and deposition of solid oxidation product that free *cyclo*telluropentane was formed during the condensation.

Owing to the greater solubilities of the two organic tellurichlorides, their separation from aluminium chloride was less complete than that of the corresponding bromides from aluminium bromide. In extractions of the chlorides ethyl alcohol as the third solvent was more favourable than water.

1. cyclo*Telluripentane Chlorides.*—cyclo*Telluripentane* 1 : 1-*dichloride* (VI), prepared by the dissociation method from 1-ε-chloroamyl*cyclo*telluripentane 1-chloride (compare p. 326), crystallised from carbon tetrachloride in six-sided prisms, m. p. 106—107° (Found: Te, 46·9, 46·95; Cl, 26·4. $C_5H_{10}Cl_2Te$ requires Te, 47·5; Cl, 26·4%). This dichloride was also prepared by the direct addition of a slight excess of chlorine to 1-ε-chloroamyl*cyclo*telluripentane 1-chloride.

With sodium dichromate in aqueous solution, the dichloride yielded a dichromate crystallising from hot water in rosettes of *yellow* needles, which are less photosensitive than the other complex dichromates described below.

1-ε-*Chloroamyl*cyclo*telluripentane* 1-*chloride* (IV) resembled the corresponding bromide, but was generally more soluble than the latter; it melted at 149—151° (Found: Te, 37·7; Cl, 20·8. $C_{10}H_{20}Cl_2Te$ requires Te, 37·65; Cl, 20·95%). When heated under reduced pressure, it dissociated into *cyclo*telluropentane and pentamethylene dichloride. With aqueous sodium dichromate, it gave a yellow, oily precipitate darkening on exposure to light.

Pentamethylene-$\alpha\varepsilon$-*bis*cyclo*telluripentane* 1 : 1′-*dichloride* (V) was much more soluble in the alcohols than the corresponding bromide; it crystallised from ethyl alcohol, containing hydrochloric acid, in anhydrous prisms, decomp. 224—225° (Found: Te, 47·3; Cl, 13·3. $C_{15}H_{30}Cl_2Te_2$ requires Te, 47·5; Cl, 13·2%). The aqueous solution gave at first a faint precipitate with silver nitrate, which slowly increased.

The mother-liquor from the crystallisation of the complex dichlorides, when precipitated fractionally with aqueous sodium dichromate, gave in succession two deposits. The second was crystalline and consisted of *pentamethylene-αε-bis*cyclo*telluripentane* 1 : 1′-*dichromate*, which crystallised from hot water in rosettes of daffodil-yellow plates, turning brown at 160° and decomposing at 193° (Found : Te, 36·2. $C_{15}H_{30}O_7Te_2Cr_2,H_2O$ requires Te, 36·5%). This dichromate was very sensitive to light, rapidly becoming brown on exposure.

2. cyclo*Telluripentane Bromides.*—cyclo*Telluripentane* 1 : 1-*dibromide* (VI), obtained as a by-product in the condensation between aluminium telluride and αε-pentamethylene dibromide, was more conveniently prepared by heating either of the two following substances to 160—190° under 25—30 mm. pressure. Thermal dissociation led to *cyclo*telluropentane and pentamethylene dibromide, with elimination of water in the case of the hydrated telluribromide. The cooled yellow distillate was diluted with carbon tetrachloride and treated with bromine in excess; *cyclo*telluripentane dibromide then slowly separated and was crystallised successively from benzene and carbon tetrachloride (yield, 90%) (Found: Te, 35·3; Br, 44·75; C, 16·8; H, 3·1. $C_5H_{10}Br_2Te$ requires Te, 35·7; Br, 44·7; C, 16·8; H, 2·8%).

*cyclo*Telluripentane 1 : 1-dibromide crystallised from carbon tetrachloride in pale greenish-yellow prisms or from light petroleum in hexagonal plates; it melted at 105—107°. It dissolved readily in benzene, chloroform, or acetone, but only sparingly in cold alcohol, carbon tetrachloride, or light petroleum. Hot water hydrolysed the dibromide, giving an acid solution, but nothing separated on cooling.

*cyclo*Telluripentane 1 : 1-dibromide was also formed by mixing carbon tetrachloride solutions of 1-ε-bromoamyl*cyclo*telluripentane 1-bromide and bromine (1·6 mols.). A heavy, red oil separated, from which petroleum or methyl alcohol extracted the dibromide.

1-ε-*Bromoamyl*cyclo*telluripentane* 1-*bromide* (IV) was readily soluble in oxygenated organic solvents, in chloroform and in water. The aqueous solution was faintly acid to litmus and gave an immediate precipitate with silver nitrate. This telluripentane bromide crystallised from acetone in colourless, oblong plates, m. p. 143—145°, resolidifying at 147° (Found : Te, 29·75; Br, 36·8; C, 27·9; H, 4·9. $C_{10}H_{20}Br_2Te$ requires Te, 29·8; Br, 37·4; C, 28·1; H, 4·7%).

*Pentamethylene-αε-bis*cyclo*telluripentane* 1 : 1′-*dibromide* (V) was readily soluble in water, less soluble in the alcohols, and almost insoluble in other organic solvents; it crystallised in colourless needles containing $1H_2O$ and decomposed at 223—224° (Found for hydrate : C, 27·75; H, 5·1. $C_{15}H_{30}Br_2Te_2,H_2O$ requires C, 28·0; H, 5·0%. Found for dried salt : Te, 40·55, 40·8; Br, 25·3. $C_{15}H_{30}Br_2Te_2$ requires Te, 40·8; Br, 25·6%).

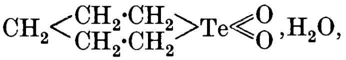
The aqueous solution of the complex dibromide was neutral to litmus and gave with silver nitrate a faint precipitate which rapidly increased.

*Pentamethylene-αε-bis*cyclo*telluripentane* 1 : 1′-*bisperbromide*, $C_5H_{10}[Te(C_5H_{10})Br_3]_2$. Bromine (2·2 mols.) in carbon tetrachloride was added to a suspension of the foregoing compound in chloroform, and the mixture heated for 30 minutes. The colour of bromine faded rapidly with the separation of a dark red oil which solidified on cooling; m. p. 102—104° (Found : Te, 26·3; Br, 49·9. $C_{15}H_{30}Br_6Te_2,H_2O$ requires Te, 26·5; Br, 49·8%). This product was insoluble in all organic media except acetone, in which it decomposed with generation of a lachrymatory vapour (possibly that of bromoacetone).

3. cyclo*Telluropentane.*—Potassium metabisulphite (25 g.), dissolved in 150 c.c. of water, was added in two equal portions, with a 20 minutes' interval, to 20 g. of powdered *cyclo*telluripentane 1 : 1-dibromide, the mixture being well stirred. The dibromide changed gradually to a dark red oil. After being shaken for 1½ hours, the oily mixture was extracted with chloroform, the dried extract evaporated in a current of hydrogen to remove the solvent and distilled under reduced pressure, and the distillate rectified with the exclusion of air (Found : Te, 64·0, 64·3; C, 30·0, 30·7; H, 5·3, 5·2. $C_5H_{10}Te$ requires Te, 64·5; C, 30·4; H, 5·1%).

Although very little tellurium was eliminated during the reduction of the dibromide, yet a considerable proportion of red, non-volatile residue was left after distillation of the *cyclo*telluropentane; this residue, which blackened on heating, was not investigated further.

cyclo*Telluropentane* was thus obtained as a lemon-yellow oil having an extremely unpleasant alliaceous odour recalling that of trimethylstibine; it boiled at 82—83°/12 mm. and at 44—45°/1—2 mm. It was oxidised rapidly in air to a colourless solid and reacted violently with fuming nitric acid. When kept for several weeks in a sealed tube, it gradually assumed a reddish-orange colour, the change being accelerated by light.

cyclo*Telluripentane* 1 : 1-*dioxide*,  $CH_2{<}^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CH_2}{>}Te{\leqslant}^{O}_{O},H_2O$, was obtained as a white, amorphous powder on addition of hydrogen peroxide to *cyclo*telluropentane dissolved in warm methyl alcohol (Found : Te, 50·3. $C_5H_{10}O_2Te,H_2O$ requires Te, 51·5%).

This insoluble product, which exploded on rapid heating, darkened at about 195° ; it had the properties of a tellurone, liberated chlorine from hydrochloric acid, decolorised warm acidified permanganate, and decomposed violently on treatment with concentrated nitric or sulphuric acid.

4. cyclo*Telluripentane Di-iodides.*—Aluminium telluride (5·5 g.) and αε-pentamethylene di-iodide (22 g.; 1·8 mols.) interacted smoothly when heated at 135—145° for 1 hour. The product was cooled and extracted with (*a*) benzene, (*b*) acetone, (*c*) methyl alcohol, and (*d*) water, leaving a black, insoluble residue (0·75 g.). The yields of (IV), (V), and (VI) were 3·5 g., 3·4 g., and 1·7 g., respectively, 4·5 g. of pentamethylene di-iodide being recovered unchanged.

1-ε-*Iodoamyl*cyclo*telluripentane* 1-*iodide* (IV) crystallised in colourless flakes, melted at 135—136°, resolidified almost immediately, and remelted at 197—198°. It dissolved slightly in hot water, giving a neutral solution (Found: I, 48·2. $C_{10}H_{20}I_2Te$ requires I, 48·7%).

Pentamethylene-αε-*bis*cyclo*telluripentane* 1 : 1′-*di-iodide* (V) crystallised from hot water in rosettes of brownish-yellow, acicular prisms, m. p. 216—217° (decomp.). It dissolved in boiling water to give an alkaline solution (Found: I, 35·6. $C_{15}H_{30}I_2Te_2$ requires I, 35·3%). Aqueous solutions of both these iodides give a transient yellow coloration with silver nitrate and no immediate precipitation of silver iodide. A slow precipitation occurs on boiling, the speed of this being greater in the case of the latter compound. Both compounds resemble the corresponding chlorides and bromides, but their solubilities are considerably less.

cyclo*Telluripentane* 1 : 1-*di-iodide*, obtained as a by-product in the foregoing condensation, is prepared preferably by adding iodine in slight excess to *cyclo*telluropentane in carbon tetrachloride. The product was obtained in two kinds of crystals: (α) Deep red prisms with purple-blue reflex (Found: Te, 28·1%); (β) highly refractive, slender, orange prisms (Found: I, 55·9. $C_5H_{10}I_2Te$ requires Te, 28·2; I, 56·2%). On exposure to light the orange form, which separated from hot solutions, was transformed into the dark red crystals within 2 days. A slower change took place in the dark. Molecular-weight determinations in hot and in cold benzene gave *M* (cryoscopic) 414, 418; (ebullioscopic) 453, 465, 473 ($C_5H_{10}I_2Te$ requires *M*, 451).

These data exclude polymerism, whereas the deepening of colour which occurred when the solutions of the di-iodides were heated suggests that the difference between the two modifications goes further than dimorphism. More experimental work would, however, be required to establish that the difference is a case of isomerism.

Dr. T. V. Barker has kindly supplied the following additional information regarding the two differently coloured forms : "Neither modification is suitable for exact angular measurements. Under the polarising microscope, the stable modification (with purple-blue reflex) is strongly dichroic, appearing light or dark red, according as the vibrations are along or across the direction of elongation. A biaxial figure is seen in convergent light with one optic axis nearly normal to the predominant face. The needles of the yellow modification show a corresponding light and dark yellow dichroism. The extinction also is straight with negative elongation, but no optic figure is visible."

The two forms of *cyclo*telluripentane 1 : 1-di-iodide were less soluble than the corresponding chloride or bromide. Both varieties melted at 135—136°, the purple crystals first becoming orange at 105°. A benzene or carbon tetrachloride solution of either form became reddish-orange on boiling and resumed a light orange tint on cooling.

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