

CXL.—*Interactions of Tellurium Tetrachloride and Aryl Alkyl Ethers. Part II.*

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THE interaction of tellurium tetrachloride and anisole is first mentioned in a communication by Michaelis (*Ber.*, 1897, **30**, 2821) on organic compounds containing inorganic radicals, where he refers to the ready introduction of the bivalent radicals SeCl_2 and TeCl_2 into various classes of organic substances. Aromatic derivatives of the former radical had been previously described by one of his pupils, Kunckell (*Ber.*, 1895, **28**, 609), and Michaelis was then announcing the discovery of an analogous series of tellurium derivatives, the work of Rust, another collaborator in the Rostock laboratories (*Ber.*, 1897, **30**, 2828).

By warming together tellurium tetrachloride (1 mol.) and anisole (2 mols.), Rust obtained a yellow compound to which, from his analyses given in duplicate, he gave the name "dichlorotelluroanisole" with formula $\text{TeCl}_2(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3)_2$. This substance was purified from crude material by transforming the latter into dihydroxide, $(\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4)_2\text{Te}(\text{OH})_2$, and regenerating the dichloride with hydrogen chloride.

From this dihydroxide Rust also prepared the dibromide, $\text{TeBr}_2(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3)_2$, di-iodide, $\text{TeI}_2(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3)_2$, dinitrate, $(\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4)_2\text{Te}(\text{NO}_3)_2$, and chloroplatinate,
 $(\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4)_2\text{TeCl}_2, \text{PtCl}_4$.

The subject was next taken up by Rohrbaech (*Annalen*, 1901, **315**, 9), who referred to the dissimilarities observable in the behaviour of selenium tetrachloride and tellurium tetrachloride as regards their condensations with aryl alkyl ethers. In the former case two substances were obtained, bisanisyl selenide and bisanisyl selenidichloride, whereas in Rust's experiments bisanisyl telluridichloride was the sole product.

In order, therefore, to obtain bisanisyl telluride, Rohrbaech removed chlorine from Rust's alleged dichloride with zinc dust in benzene and obtained a highly coloured compound which he stated was "*p*-telluroanisole," $\text{Te}(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3)_2$. He also converted this alleged monotelluride, by suitable treatment with chlorine, bromine, and dilute nitric acid, respectively, into Rust's dichloride, dibromide and dinitrate.

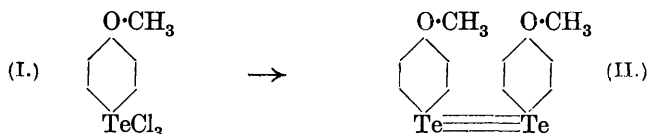
Fourteen years later, Rohrbaech's supposed bis-*p*-anisyl telluride, $\text{Te}(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3)_2$, was examined by Lederer (*Ber.*, 1915, **48**, 1424), who prepared its mercurichloride, mercuribromide, and mercuriodide, $\text{C}_{14}\text{H}_{14}\text{O}_2\text{TeHgX}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$). Lederer also obtained

(*loc cit.*, p. 2053) by the action of methyl iodide on Rohrbach's telluride a product yielding anisoledimethyltellurium picrate. But the conclusions which he drew from this methylation have, however, been already shown to be groundless and a complete explanation of the reaction has been given in the previous paper on this subject (Morgan and Drew, J., 1925, 127, 2310).

In a subsequent paper, Lederer (*Ber.*, 1916, 49, 1076) obtained the true bis-*p*-anisyl telluride by the interaction of tellurium dibromide and magnesium *p*-anisyl bromide and converted this telluride into dichloride, dibromide, di-iodide, and oxide. The whole para-series differed essentially from the corresponding derivatives of Rohrbach's telluride made either by that investigator, or by Rust or by Lederer himself. Later, Lederer prepared the corresponding members of the meta- and ortho-series, again using the Grignard reaction but with the appropriate magnesium *m*- or *o*-anisyl iodide (*Ber.*, 1919, 52, 1989; 1920, 53, 712), and since these two series also differed from Rohrbach's presumably isomeric series it followed by exclusion that, in the Rust-Rohrbach preparations, tellurium had been introduced into the side chain, thus giving the formula $\text{Br}_2\text{Te}(\text{CH}_2\cdot\text{O}\cdot\text{C}_6\text{H}_5)_2$. But this conclusion is fallacious, because the original assumption of isomeric relationship between the Rust-Rohrbach and Lederer series of compounds is incorrect.

The researches described in the present communication furnish a correct explanation of the foregoing differences.

The compound first handled by Rust was not dichlorotelluro-bisanisole, $\text{Cl}_2\text{Te}(\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3)_2$, but *p*-anisyltelluritrichloride (I), and accordingly its highly coloured reduction product obtained by Rohrbach with complete elimination of chlorine was not a bisanisyl telluride $(\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_5-\text{H})_2\text{Te}$, but *bis-p*-anisyl ditelluride (II).



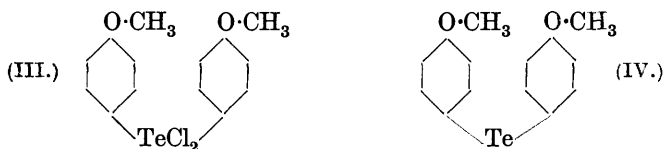
Hence Lederer's discussion of the constitution of Rohrbach's assumed bisanisyl telluride is irrelevant, inasmuch as he was not even dealing with an isomeric of his three *o*-, *m*-, and *p*-bisanisyl tellurides.

Our experiments show conclusively that *p*-anisyltelluritrichloride (I) is the sole product of the interaction of tellurium tetrachloride (1 mol.) and anisole (3 mols.) in warm chloroform, the yield being quantitative. In the preparations made by Rust and by Lederer the reagents were heated together without solvent on the water-bath, but on repeating their experimental conditions we again

obtained *p*-anisyltelluritrichloride as the sole product. The yellow colour of the substance and its mode of hydrolysis together with complete analytical data confirm our conclusions as to its constitution (I).

On reduction with potassium metabisulphite, the trichloride gave a quantitative yield of bis-*p*-anisyl ditelluride (II), obtained in dark brownish-red crystals with green, metallic lustre. In its intense colour this ditelluride resembles Lederer's bisphenyl ditelluride (*Ber.*, 1915, 48, 1345), which is described as separating in blood-red crystals. Further evidence for the composition of bis-*p*-anisyl ditelluride (II) is afforded by molecular-weight determination and by the large tellurium content of the compound.

It now remained to prepare the true *bis-p-anisyltelluridichloride* (III) and this was accomplished by heating tellurium tetrachloride with excess of anisole at 150–180°; this dichloride was then obtained in practically quantitative yield.



This dichloride (III), unlike the trichloride (I), is colourless and reducible only with difficulty, but when the chlorine is removed entirely with zinc dust, the product, *bis-p-anisyl telluride* (IV), is also colourless. As already pointed out in earlier papers on organic tellurium compounds, these colour differences are themselves a useful guide to the constitution of tellurium derivatives (Morgan and Drew, J., 1925, 127, 531, 2307).

Having thus established the nature of the tellurium anisyl derivatives, we made comparative experiments on the next homologues of anisole and found that the formation of telluritrichlorides took place most readily with *o*-tolyl methyl ether, and the resulting yellow *2-methoxytolyl-5-telluritrichloride* was reducible to the intensely coloured *bis-2-methoxy-5-tolyl ditelluride*. Telluritrichlorides were obtained, but with greater difficulty, from *m*- and *p*-tolyl methyl ethers.

Addendum. Interaction of Tellurium Tetrachloride and the Homologues of Acetic Anhydride.

During this collaboration, experiments were also made to ascertain whether the condensation found to take place between tellurium tetrachloride and acetic anhydride (Morgan and Drew, J., 1925, 127, 531) could be effected with anhydrides of the homologues of acetic acid.

The results showed that the tendency to undergo this condensation with tellurium tetrachloride fades away rapidly as the homologous series is ascended.

Trichlorotelluripropionic acid obtained from propionic anhydride was reducible to *ditellurodipropionic acid*. With *n*-butyric anhydride, tarry products predominated and only a very little of the telluriferous butyric acid was observed. With *isovaleric* anhydride, a considerable proportion of the tetrachloride was reduced with elimination of tellurium.

EXPERIMENTAL.

Condensation of Tellurium Tetrachloride and Anisole.

1. *Interaction in Chloroform.*—Tellurium tetrachloride (2 g.), 2.4 g. of anisole, and 30 c.c. of dry chloroform were heated on the water-bath for 2 hours. The mixture became yellowish-red even in the cold, but on warming hydrogen chloride was evolved copiously and the condensation product crystallised to a mass of yellow needles. No tellurium was evolved and the condensation proceeded quantitatively. The crude product melted at 190° and gave Cl, 30.7% (Calc. for di- and tri- chlorides, Cl, 17.2 and 31.2, respectively).

In contact with water, this crude yellow trichloride was hydrolysed to a white hydroxide. When treated with cold aqueous potassium metabisulphite ($2\frac{1}{2}$ mols.), the hydroxide was reduced to an insoluble dark red product which on crystallisation from dilute alcohol melted at 57° and gave Te, 56.8% (Calc. for dianisyl monotelluride and ditelluride, Te, 37.3 and 54.8 respectively).

The foregoing analyses, even when effected on the crude products of reaction, show that in chloroform, tellurium tetrachloride and anisole (3 mols.) yield an anisyltelluritrichloride which on reduction furnishes dianisyl ditelluride.

2. *Condensation without Solvent* (Method of Rust and Lederer).—The trichloride obtained by the foregoing procedure was apparently identical with Rust's "dichlorotelluroanisole," although our analysis indicated a trichloride. As the solvent used in our experiments may have modified the reaction, we repeated the condensation according to Rust's recipe, which is practically identical with the method adopted by Lederer (*loc. cit.*). The crude products in two preparations melted at 195° and 190° and after one crystallisation from dry chloroform gave Cl, 29.8 and 30.9%, whereas the di- and tri-chlorides require, respectively, Cl, 17.2 and 31.2%.

Reduction of the foregoing products of the dry process with ice-cold aqueous potassium metabisulphite furnished a substance which crystallised from warm alcohol, on addition of water, in dark red,

glistening crystals, m. p. 57°. Reduction with zinc dust in benzene led to a dark red oil, the alcoholic solution of which yielded a dark red substance melting at 49—51°, a melting point corresponding with Rohrbaech's 50° and Lederer's "50° not easily observed because of the dark colour."

p-Anisylltelluritrichloride, $\text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{TeCl}_3$.—On warming together tellurium tetrachloride (1 mol.) and anisole ($1\frac{1}{2}$ —2 mols.) in dry chloroform solution a practically quantitative yield of the trichloride was obtained, calculated on the tetrachloride; the product separated directly in a nearly pure condition. Dry chloroform or ether was used for recrystallisation, the substance separating in yellow needles, m. p. 190° (Found: C, 24.3, 24.7; H, 2.3, 2.1; Cl, 31.1; Te, 37.7. $\text{C}_7\text{H}_7\text{OCl}_3\text{Te}$ requires C, 24.6; H, 2.05; Cl, 31.2; Te, 37.4%).*

p-Anisylltelluritrichloride was almost insoluble in cold chloroform, benzene, or light petroleum and dissolved only moderately in the warm solvents. With water and moist solvents, it decomposed to a white hydroxide; it dissolved completely in hydrochloric acid or aqueous caustic soda.

Acetic acid added to a solution of 2 g. of *p*-anisylltelluritrichloride in 2*N*-sodium hydroxide precipitated a white amorphous powder having no definite melting point. Dissolution in alkali and precipitation with acetic acid were repeated; the amorphous product, after drying, gave C, 28.4; H, 2.6; whereas a trihydroxide, $\text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{Te}(\text{OH})_3$, would require C, 29.4; H, 3.5%. As the substance was insoluble in ordinary solvents and uncrystallisable, it was not investigated further. For a product obtained under essentially the same conditions Rust obtained Te, 33.55, 33.60; C, 44.37, 44.46; H, 4.34, 4.33%, corresponding with a di-*p*-anisylltelluridihydroxide, $(\text{CH}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4)_2\text{Te}(\text{OH})_2$. Two other carbon and hydrogen determinations confirmed the lower values for these elements, and a portion of the hydroxide when evaporated with concentrated hydrochloric acid regenerated yellow needles of *p*-anisylltelluritrichloride (m. p. 191°. Found: Cl, 30.3; calc., Cl, 31.2%).

This hydrated oxide dissolved in warm dilute nitric acid and, on cooling, a yellowish-pink, amorphous precipitate separated (m. p. 190—210°); the filtrate yielded yellowish-white plates, identified by melting point and analysis as 2 : 4-dinitrophenol.

Bis-p-anisylditetelluride (II), obtained in almost quantitative yield

* Tellurium is most satisfactorily determined in these compounds by the Carius method (9—10 hours at 260°); the solution is evaporated to dryness with hydrochloric acid, the residue dissolved in water, and the tellurium precipitated with hydrazine hydrochloride and sulphurous acid.

on adding gradually potassium metabisulphite to *p*-anisyltelluritrichloride suspended in ice-water, crystallised from dilute alcohol or petroleum (b. p. 40—60°) in reddish-brown crystals. From its more concentrated solution in benzene the ditelluride separated in highly lustrous, green crystals (Found: C, 35·6; H, 3·0; Te, 54·2; *M*, cryoscopic in benzene, 472·5. C_7H_7OTe requires C, 35·8; H, 3·0; Te, 54·4%. $C_{14}H_{14}O_2Te_2$ requires *M*, 469).

The ditelluride oxidised slowly in air to a yellowish-grey substance, and its alcoholic solution was at once decolorised by hydrogen peroxide; a white, amorphous product was obtained on concentrating the liquid. On passing chlorine through its chloroform solution, the colour changed and *p*-anisyltelluritrichloride crystallised out (m. p. 192°). Bromine in similar circumstances yielded *p*-anisyltellurtribromide, separating in orange-yellow crystals, m. p. 187·5° (Rust's dibromotelluroanisole melted at 183—185°). This tribromide was hydrolysed by water to the white hydroxide and with metabisulphite it regenerated the di-*p*-anisyl ditelluride. On adding aqueous mercuric chloride to the ditelluride in ethereal solution, a light brown mercurichloride was precipitated.

Di-p-anisyltelluridichloride (III).—Tellurium tetrachloride (15 g.) and 30 g. of anisole (5 mols.) were heated for 24 hours at 150—180°, the solution being afterwards allowed to solidify in a vacuum. The yield of crystalline product was 95% of the theoretical. The dichloride crystallised from benzene-petroleum (b. p. 40—60°) in colourless prisms, often retaining a slightly pink tinge; it melts at 181—182° (Found: C, 40·5; H, 3·6; Cl, 17·25; Te, 30·9. $C_{14}H_{14}O_2Cl_2Te$ requires C, 40·7; H, 3·4; Cl, 17·2; Te, 30·9%). The dichloride was insoluble in water, although slightly hydrolysed by this solvent; it was completely hydrolysed by aqueous sodium hydroxide, but dissolved only sparingly in excess of this alkali. It was not readily reduced, being resistant to the action of metabisulphite and only attacked with difficulty by zinc dust.

Bis-p-anisyl Telluride (IV).—Di-*p*-anisyltelluridichloride (10 g.) and 5 g. of zinc dust in 150 c.c. of benzene were heated for 24 hours under reflux. Some tar separated and the filtered solution was concentrated. The white crystals which separated still contained chlorine and were subjected to the action of more zinc dust until all the halogen was eliminated. The halogen-free compound (yield 37%) crystallised from dilute alcohol in colourless, nacreous plates, m. p. 53—54° (Found: C, 49·0; H, 4·2; Te, 37·6. $C_{14}H_{14}O_2Te$ requires C, 49·2; H, 4·1; Te, 37·3%).

On mixing chloroform solutions of the telluride and bromine, di-*p*-anisyltelluridibromide separated in sulphur-yellow crystals,

m. p. 190°; the bromo-derivative of Rohrbaech's ditelluride was described as orange-yellow.

2-Methoxytolyl-5-telluritrichloride, $\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{CH}_3)\cdot\text{TeCl}_3$.—Four g. of tellurium tetrachloride (1 mol.) and 3.7 g. of *o*-tolyl methyl ether (2 mols.) in 30 c.c. of dry chloroform were heated together on the water-bath; hydrogen chloride was evolved and, after one hour, yellow needles separated (Found: Cl, 29.6. $\text{C}_8\text{H}_9\text{OCl}_3\text{Te}$ requires Cl, 30.0%). The product was only very sparingly soluble in ordinary organic media with the exception of acetone, but when separating from this solvent after the addition of light petroleum, the crystals obtained were progressively whiter and showed a diminution in the percentage of chlorine.

These decomposition products were extracted with chloroform and the filtered solution was saturated with hydrogen chloride. A deposit of pale yellow needles was formed melting to a red liquid at 232–233° (Found: Cl, 30.0%).

The trichloride was insoluble in cold water, but hydrolysed, on warming, to a white hydroxide which dissolved readily in benzene or chloroform. With potassium metabisulphite, the trichloride was reduced to a highly coloured ditelluride.

A large excess of *o*-tolyl methyl ether and tellurium tetrachloride with a little dry chloroform were gradually heated to 170°; the solid product was filtered from unchanged ether and extracted under reflux with chloroform, but no soluble dichloride was obtained.

Bis-2-methoxy-m-tolyl Ditelluride, $\{\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{CH}_3)\cdot\text{Te}\}_2$.—To 5 g. of the preceding trichloride in 50 c.c. of ice-cold water were added slowly 9.5 g. of potassium metabisulphite (3 mols.); the reduction proceeded rather more slowly than in the case of the anisyl derivative, the colour changing from yellow to black. After stirring occasionally for an hour, the black residue was extracted with ether. The dark red solution deposited dark needles, which recrystallised from petroleum (b. p. 40–60°) in similar forms with a brownish-green bronzy lustre; m. p. 77–78° (Found: C, 38.6; H, 3.6; Te, 51.5; *M*, cryoscopic in benzene, 493. $\text{C}_8\text{H}_9\text{OTe}$ requires C, 38.6; H, 3.6; Te, 51.3%. $\text{C}_{18}\text{H}_{18}\text{O}_2\text{Te}_2$ requires *M*, 497).

This ditelluride was very soluble in benzene, chloroform, acetone or ether, but only sparingly soluble in cold alcohol or petroleum (b. p. 40–60°), dissolving more readily on warming. From its alcoholic solution, water precipitated a bright red emulsion which solidified to a dark green, crystalline mass. Hydrogen peroxide instantly decolorised the alcoholic solution. Chlorine passed into the chloroform solution regenerated 2-methoxytolyl-5-telluritrichloride; bromine under similar conditions combined additively to form the corresponding orange-yellow *tribromide*.

4-Methoxytolyl-3-telluritrichloride.—*p*-Tolyl methyl ether and tellurium tetrachloride did not interact appreciably in chloroform solution, but at higher temperatures condensation took place. Equal parts of the tetrachloride and *p*-tolyl ether with a trace of chloroform were heated on the water-bath until hydrogen chloride was no longer evolved. The resulting yellow liquid slowly yielded greenish-yellow crystals, which underwent partial hydrolysis in such solvents as moist benzene, chloroform and acetone. Accordingly these products were redissolved in dry chloroform and the pale yellow solution was saturated with hydrogen chloride. On concentrating the liquid in a vacuum desiccator, well-defined, yellow, rectangular plates separated, m. p. 135° (Found: Cl, 29.6. $C_8H_9OCl_3Te$ requires Cl, 30.0%). The reduction of this and the following trichloride proceeded less readily than that of their foregoing isomeride.

3-Methoxytolyl-(4 or 6)-telluritrichloride.—Equal parts of tellurium tetrachloride and *m*-tolyl methyl ether with a little chloroform were heated on the water-bath until evolution of hydrogen chloride had ceased; the oily residue was then cooled until dark green crystals separated. When the crude material was dissolved in dry chloroform and the solution saturated with hydrogen chloride, no precipitation occurred, but slow evaporation in a vacuum desiccator furnished a yellowish-brown crystalline mass, m. p. 154° (Found: Cl, 28.2. Calc., Cl, 30.0%). This trichloride is much more soluble than its isomeride in organic media, but exposure to moisture leads to considerable hydrolysis.

Condensation between tellurium tetrachloride and each of the following: β -naphthyl methyl ether, monoethyl ethers of resorcinol and quinol, monomethyl ether of quinol, led to viscid, uncrystallisable products. No appreciable interaction was observed with *p*-nitroanisole, but a preliminary experiment with *p*-bromoanisole indicated a normal condensation to a trichloride, m. p. 184°; this was reducible by aqueous metabisulphite to a dark red oily ditelluride, which was brominated in chloroform solution to an orange-yellow tribromide, m. p. 153°.

Interaction of Tellurium Tetrachloride and the Homologues of Acetic Anhydride.

Trichlorotelluripropionic Acid, $Cl_3Te \cdot CH(CH_3) \cdot CO_2H$. Five g. of tellurium tetrachloride and 7 g. of propionic anhydride (3 mols.) in 38 c.c. of chloroform were heated under reflux for 4 hours. Hydrogen chloride was evolved slowly, and 0.3 g. of tellurium eliminated. The filtered liquid was concentrated in a vacuum desiccator, and chloroform added; a brown solid then separated (yield 4 g.). The product was extremely soluble in all organic

media and could not be freed by recrystallisation from tarry impurities. A halogen estimation on the crude material, obtained in white plates by allowing the viscous liquid from the foregoing condensation to remain in a vacuum desiccator for 4 weeks, gave Cl, 34.7 ($C_3H_5O_2Cl_3Te$ requires Cl, 34.6%). This substance melted at 145—150° and on exposure to the atmosphere the crystals became liquid. A condensation with a large excess (6 mols.) of propionic anhydride gave a smaller yield of the trichloro-compound.

Ditellurodipropionic Acid, $\{Te \cdot CH(CH_3) \cdot CO_2H\}_2$.—Crude trichlorotelluripropionic acid was reduced with aqueous metabisulphite (2.5 mols.), and the yellow solution extracted with ether. The oily residue from the ethereal extract redissolved in chloroform to a solution which yielded a brick-red solid, m. p. 75°. The pale yellow *silver* salt was photosensitive and became brownish-black on exposure, the *copper* salt was a pale green precipitate decomposing at 175°, the soluble *potassium* salt separated from concentrated aqueous solution in brick-red plates blackening at 175°.

Tribromotelluripropionic Acid, $Br_3Te \cdot CH(CH_3) \cdot CO_2H$, resulted from the interaction of ditellurodipropionic acid and bromine in chloroform; it separated as a yellow oil which solidified to a bright yellow solid, m. p. 139—141° (Found: Br, 53.8. $C_3H_5O_2Br_3Te$ requires Br, 54.4%). This tribromo-derivative dissolved readily in ether or acetone or in warm benzene, chloroform or ethyl acetate, separating from these solutions, on addition of light petroleum, as an oil which slowly solidified. When kept in a sealed tube, the yellow tribromo-compound changed into a greenish-black decomposition product.

Tellurium tetrachloride and *n*-butyric anhydride when boiled in chloroform solution slowly evolved hydrogen chloride, but the tarry product as extracted with acetone and other organic solvents remained oily. The acidic nature of this product was demonstrated by the formation of a yellow *silver* and green *copper* salt. Bromine in chloroform gave an oily additive product. Interaction between tellurium tetrachloride and *isovaleric* anhydride was attended by elimination of a considerable proportion of tellurium. From an experiment with monochloroacetic anhydride, the greater part of the tellurium tetrachloride was recovered.

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