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ORGANIC TELLURIUM COMPOUNDS—III

THE ADDITION OF TELLURIUM DERIVATIVES TO UNSATURATED COMPOUNDS

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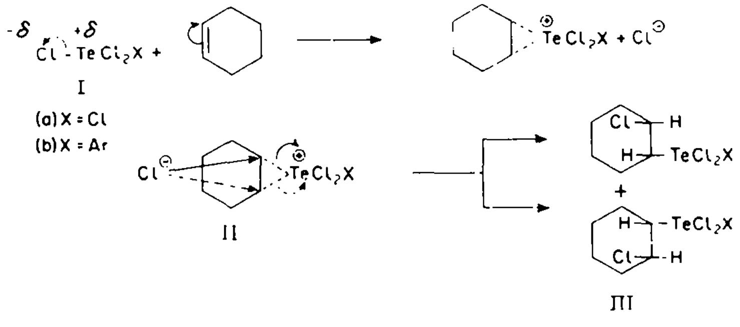
Abstract—The reaction of tellurium tetrachloride and aryltellurium trichloride with simple olefins and γ, δ-unsaturated acids has been studied. Cyclohexene gives normal products of addition while styrene, di-isobutylene and 1,4-diphenylbutadiene-1,3 do not react with aryltellurium trichlorides and give rise to elementary tellurium when treated with tellurium tetrachloride.

In the case of the unsaturated acids lactonization occurs due to the participation of the neighbouring carboxyl group.

IT was found recently[1] that tellurium tetrachloride and aryltellurium trichlorides added to cyclohexene give rise to 2-chlorocyclohexyltellurium trichloride (IIIa) and aryl-2-chlorocyclohexyltellurium dichloride (IIIb) respectively.

The mechanism of these reactions is probably via a cyclic telluronium ion intermediate* (II) which suffers a nucleophilic attack by the chloride ion, giving rise to racemic *trans* compounds.



This reaction, however, is not general since some simple olefins do not react with tellurium derivatives and others by reduction produce elementary tellurium.

In the case of cyclohexene, the reaction with aryltellurium trichloride in boiling carbon tetrachloride, yields several crystalline dichlorides of type IIIb in very good yield, but in contrast styrene, di-isobutylene and 1,4-diphenylbutadiene-1,3 do not react, the starting materials being recovered almost quantitatively.

The use of tellurium tetrachloride as electrophilic reagent shows similar differences in reactivity. Cyclohexene yields an addition compound, while styrene, di-isobutylene and 1,4-diphenylbutadiene-1,3 in carbon tetrachloride solution affect

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* Similar to the cyclic sulphonium ion proposed by Kharasch[2] in the reaction of arylsulphenyl chloride with unsaturated compounds.

[1] M. de Moura Campos and N. Petragnani, *Tetrahedron Letters* No 6, 11 (1959).

[2] N. Kharasch and M. Buess, *J. Amer. Chem. Soc.* 71, 2724 (1949); N. Kharasch and A. J. Havlik, *Ibid.* 75, 3734 (1953).

reduction of the reagent to elementary tellurium and give rise to unidentified halogenated products, while stilbene does not react even when the temperature is increased. It is interesting that Fischer and Eisner[3] observed the formation of tellurium during the reaction of cyclohexene with tellurium tetrachloride, this result being confirmed by us, but, when the reaction is carried out in carbon tetrachloride an addition product is obtained in good yield.[1]

In accordance with this observation it seemed likely that under special experimental conditions, the alkenes that promote the reduction of tellurium tetrachloride to elementary tellurium may produce 2-chloro-alkyltellurium trichlorides.

The reduction of aryltellurium trichloride with hydrated sodium sulphide[4] or with sodium bisulphite[5] generally gives rise to ditellurides.

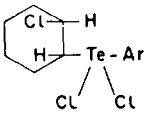
$$2ArTeCl_3 \rightarrow Ar—Te—Te—Ar$$

In a few cases trichlorides are cleaved into elementary tellurium.[6] Similarly, it has now been observed that 2-chlorocyclohexyltellurium trichloride yields tellurium.

The reaction of compounds IIIb (as *p*-ethoxy derivatives) with the agents that normally affect the transformation of tellurium dichlorides to the corresponding tellurides, has been studied.

The 2-chlorocyclohexyltellurium triiodide analogue of compound IIIa, is obtained by treating the latter with an aqueous solution of potassium iodide.*

TABLE 1. ARYL-2-CHLOROCYCLOHEXYLTELLURIUM DICHLORIDES



Ar	Yield %	M.p.	Appearance	Analyses Te calc.	Analyses Te found
p-$C_2H_5OC_6H_4$	72	121–124° (dec)	colourless plates from ethanol	26·29	26·48
C_6H_5	63	129–131° (dec)	colourless prisms from ethanol	32·45	32·72
1-$C_{10}H_7$	87	158–160° (dec)	colourless prisms from benz-pet eth	28·78	28·78
2-$C_{10}H_7$	96	136–138° (dec)	colourless needles from ethanol	28·78	28·75

Earlier studies[1,8] have shown that aryltellurium trichlorides react with γ,δ-unsaturated acids, in which the double bond is activated by carboxyl participation[9]

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* This procedure is successful for tellurium triiodides[7] in cases where the ditellurides cannot be prepared, since they are starting materials for the preparation of the latter compounds.

[3] C. H. Fischer and A. Eisner, *J. Org. Chem.* **6**, 169 (1941).

[4] L. Reichel and E. Kirchbaum *Ber. Dtsch. Chem. Ges.* **76**, 1105 (1943).

[5] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.* 2307 (1925).

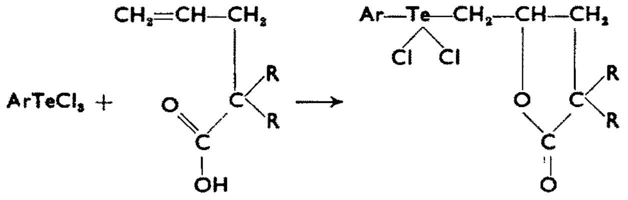
[6] L. Reichel and E. Kirchbaum, *Liebigs Ann.* **523**, 211 (1936); L. Reichel and K. Ilberg, *Ber. Dtsch. Chem. Ges.* **76**, 1108 (1943).

[7] N. Petragnani, *Tetrahedron* **11**, 15 (1960).

[8] M. de Moura Campos and N. Petragnani, *Ber. Dtsch. Chem. Ges.* **93**, 317 (1960).

[9] P. N. Craig, *J. Amer. Chem. Soc.* **74**, 130 (1952); R. T. Arnold, M. de Moura Campos and K. L. Lindsay, *Ibid.* **75**, 1044 (1953).

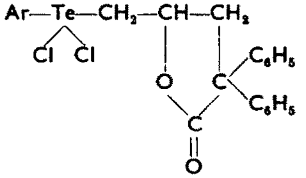
giving rise to δ-aryldichlorotelluro-γ-valerolactones (V). Due to the neighbouring group effect, only mild conditions need be employed.



IV V

The mechanism of this cyclization involving a cyclic oxonium ion intermediate is similar to that proposed by Arnold *et al.*[9] for the addition of bromine to unsaturated, type IV compounds. Table 2 gives a list of compounds of type V which have been prepared.

TABLE 2. 2,2-DIPHENYL-5-(ARYLDICHLOROTELLURIUM)-4-PENTANELACTONS

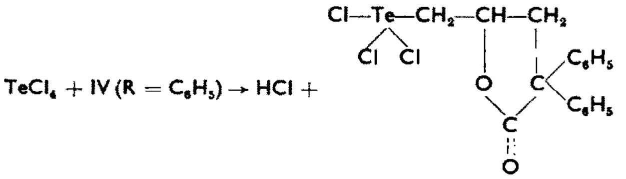


Ar	Yield %	M.p.	Appearance	Analyses Te calc.	Analyses Te found
p-$C_6H_5OC_6H_4$	80 100^{+}	122–125°	colourless needles from benz–meth.	20·61	20·10
C_6H_5	90	188–189°	colourless needles from benz–pet ether	24·21	24·24
1-$C_{10}H_7$	75	209–211°	colourless needles from benz–meth.	22·11	22·28

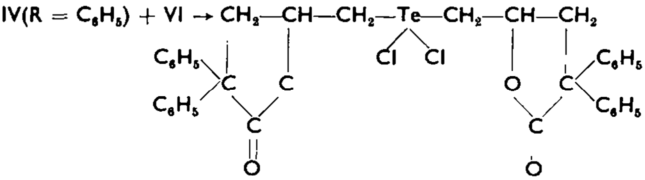
(+)-Prepared by method (B)

In the reaction of tellurium tetrachloride with 2,2-diphenyl-penten-4-oic acid (IV; R = C_6H_5), equimolar proportion of the reagents produce a white viscous residue from which no definite substance was isolated. On the other hand, using molar proportions of 2:1, the di-[5-(2,2-diphenyl-4-valerolactone)]-tellurium dichloride (VII) is formed.

This result is in accordance with the increased reactivity of double bonds activated by carboxyl participation, since the possible trichloride intermediate (VI) reacts with excess of the unsaturated compound producing the dichloride (VII).

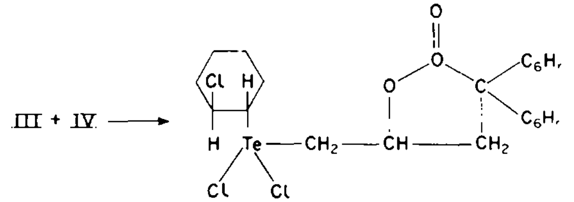


VI

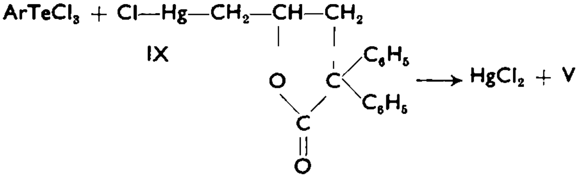


VII

Although 2-chlorocyclohexyltellurium trichloride is stable in excess of cyclohexene, this trichloride reacts with IV (R = C_6H_5) producing 2-chlorocyclohexyl-[5-(2,2-diphenyl-4-valerolactone)]-tellurium dichloride (VIII). The structure of the cyclic tellurium dichlorides V and VII were confirmed by preparation in accordance with the method of Rheinboldt and Vicentini[10] starting with 2,2-diphenyl-5-chloromercury-pentanolactone (IX).*



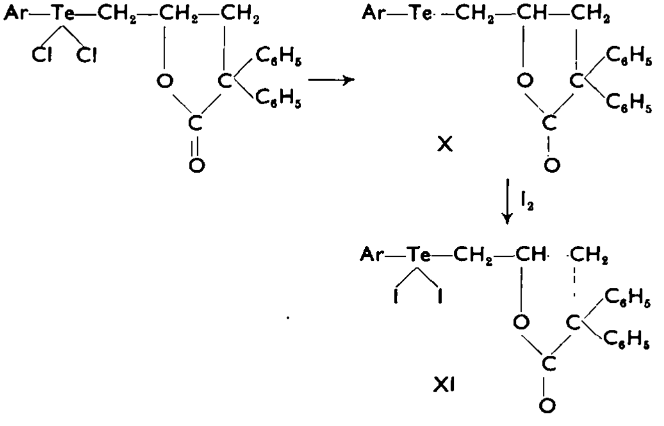
VIII



IX

$$TeCl_4 + 2IX \rightarrow VII$$

In contrast with the reduction of dichlorides IIIb, the aryl-lactonic dichlorides give rise to the expected tellurides (X) which were isolated and identified as the diiodides (XI).[8]



X

XI

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* The m.p. of this mercury compound (IX) is 175–178° and not as given by Rowland and Perry.[11]

[10] H. Rheinboldt and G. Vicentini, *Ber. Dtsch. Chem. Ges.* **89**, 624 (1956); G. Vicentini, *Ibid.* **91**, 801, (1958).

[11] R. L. Rowland, W. L. Perry and H. L. Friedman, *J. Amer. Chem. Soc.* **73**, 1040 (1951).

Under drastic conditions the reduction results in diarylditellurides similar to the results with derivatives of acetone and acetophenone.[12]

EXPERIMENTAL

Aryl-2-chlorocyclohexyltellurium dichlorides (Table 1)

p-phenoxyphenyl-2-chlorocyclohexyltellurium dichloride (III; $X = p\text{-}C_6H_5\text{—}O\text{—}C_6H_4$). *p*-phenoxyphenyltellurium trichloride (0·80 g; 0·002 mole) was refluxed in 10 cc cyclohexene for 1 hr and then heated in an open vessel in the presence of excess ethanol to remove cyclohexene and precipitation of the dichloride in crystalline form.

Similarly the phenyl derivative was prepared from phenyltellurium trichloride (0·62 g; 0·002 mole) and 30 cc cychlohexene after 3 hr reaction.

1-*Naphthyl-2-chlorocyclohexyltellurium dichloride* (III: $X = 1\text{-}C_{10}H_7$). A mixture of 1-naphthyltellurium trichloride (0·54 g; 0·0015 mole), and 20 cc cyclohexene were refluxed for 2 hr with separation of the crystalline dichloride.

Similarly, the 2-naphthyl derivative was prepared.

Attempted reaction of p-*ethoxyphenyltellurium trichloride with other olefins*

A mixture of *p*-ethoxyphenyltellurium trichloride (0·72 g; 0·002 mole) and styrene (0·30 g 0·003 mole) in 15 cc chloroform was refluxed for 12 hr. After addition of pet ether (50–70°) the trichloride was recovered unchanged. Similar results were obtained using glacial acetic acid and a large excess of styrene.

The reaction with 1,4-diphenylbutadiene-1,3 in carbon tetrachloride gave the same negative results.

A mixture of the trichloride (0·72 g; 0·002 mole) and 10 cc of di-isobutylene (Eastman Organic Chemicals P 2125; b.p. 98—100°) was refluxed for 40 min, the unchanged trichloride being recovered.

Reactions of tellurium tetrachloride with other olefins

During the reaction of tellurium tetrachloride with diisobutylene heat was evolved, and elementary tellurium separated. Similar results were obtained by reaction in carbon tetrachloride.

Mixing equimolar amounts of tellurium tetrachloride and styrene in carbon tetrachloride resulted in a yellow solution with evolution of heat. This solution boiled or evaporated *in vacuo* gave rise to a viscous black product from which no definite compound was isolated.

Tellurium tetrachloride (1 mole) was reduced to tellurium by addition of a solution of 1,4-diphenylbutadiene-1,3 (2 moles) in carbon tetrachloride. This reduction is accelerated by heat. By evaporation of the filtrate an oily residue was formed which partially crystallized on addition of ethanol. This product, free from tellurium and containing halogen, m.p. about 100° could not be purified.

Reduction of 2-chlorocyclohexyltellurium trichloride and p-*ethoxyphenxyl-2-chlorocyclohexyltellurium dichloride*

Reduction of the trichloride and the dichloride with hydrated sodium sulphide, sodium bisulphite, and hydrazine sulphate produced elementary tellurium.

2-*Chlorocychlohexyltellurium triiodide*

A solution of 2-chlorocyclohexyltellurium trichloride (0·70 g; 0·002 mole) in a small volume of ethanol was treated with excess aqueous potassium iodide. The red triiodide crystallized by addition of small amounts of benzene; yield 1·10 g; (88%). Black reddish brilliant needles were obtained from a mixture of benzene and pet ether (50–70°), m.p. 175–190°(dec.). (Found: Te, 20·38; Calc. for $C_6H_{10}ClI_3Te$: Te, 20·76%).

2,2-*Diphenyl*-5-(*aryldichlorotellurium*)-4-*pentanolactone* (V) Table 2

2,2-*Diphenyl*-5-(p-*phenoxyphenyl-dichlorotellurium*)-4-*pentanolactone*. (A) *p*-phenoxyphenyltellurium trichloride (0·80 g; 0·002 mole) was treated with a solution of 2,2-diphenyl-penten-4-oic acid

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[12] N. Petragnani, *Tetrahedron* **12,** 219 (1961).

(0·50 g; 0·002 mole) in 40 cc chloroform. The resulting yellow solution looses its colour slowly with evolution of hydrogen chloride. After 4 hr the chloroform was removed by heating with ethanol and on cooling the crystalline colourless dichlorotellurolactone separated. The phenyl and 1-naphtyl derivatives were similarly prepared.

(B) a solution of 2,2-diphenyl-5-chloromercury-4-pentano lactone (1·12 g; 0·0025 mole) and *p*-phenoxyphenyltellurium trichloride (1·00 g; 0·0025 mole) in 5 cc pure dioxane were refluxed for 1 hr on cooling, the mercuric chloride-dioxane complex precipitated, and was filtered off. The filtrate was added to 50 cc of 2% HCl yielding the crystalline dichloride. 1·54 g (quantitative yield). By crystallization from benzene and pet ether (50–70°) colourless needles were obtained m.p. 122–125°. A mixed m.p. with the dichloride obtained in (A) was not depressed.

Similarly the *p*-methoxyl derivative was prepared in quantitative yield.

2,2-(0,0′-*Diphenyleny*)-5-(p-*ethoxyphenyl-dichlorotellurium*)-4-*pentanolactone*. A solution of *p*-ethoxyphenyltellurium trichloride (0·72 g; 0·002 mole) and 9-allyl-9-fluorene carboxylic acid (0·050 g; 0·002 mole) in 30 cc chloroform was refluxed for 2½ hr with evolution of hydrogen chloride and decolourization of the yellow solution. The crystalline colourless dichlorotellurolactone was formed as in the preceeding experiment, wt: 0·66 g (yield 58%). The product crystallized from benzene and pet ether (50–70°) in colourless needles m.p. 206–209° (dec). (Found: Te, 22·33; Calc. for $C_{25}H_{22}O_3Cl_2Te$: Te 22·42%).

Di-5-(2,2-*diphenyl*-4-*pentanolactone*) tellurium dichloride VII. (A) A solution of tellurium tetrachloride (0·54 g; 0·002 mole) and 2,2-diphenyl-penten-4-oic acid (1·00 g; 0·004 mole) in 3 cc purified dioxane was refluxed for 2 hr with evolution of hydrogen chloride and initial decolourization. The resulting dark solution was cooled and added to 100 cc 2 % HCl with separation of a white viscous product which slowly solidified, wt: 1·40 g (quantitative yield). The crude dichloride was crystallized first from benzene and then from methanol in colourless needles m.p. 195–198° (Found: Te, 18·28% Calc. for $C_{34}H_{30}O_4Cl_2Te$: Te, 18·20%).

(B) A solution of tellurium tetrachloride (0·67 g; 0·0025 mole) and 2,2-diphenyl-5-chloromercury-4-pentanolactone (2·24 g; 0·005 mole) in 7·5 cc pure dioxane was refluxed for 1·5 hr. After removal of the mercuric chloride-dioxane complex and addition of 2% HCl) and ethanol the viscous product was solidified wt 1·75 g (quantitative yield). The crude dichloride was purified as in (A) crystallizing in needles m.p. 195–198°. Mixed m.p. with the dichloride prepared in (A) was not depressed.

2,2-*Diphenyl*-5-(2-*chlorocyclohexyl-dichlorotellurium*)-4-*pentanolactone* (VIII). A solution of 2-chlorocyclohexyltellurium trichloride (0·70 g; 0·002 mole) and 2,2-diphenyl-penten-4-oic acid (0·50 g; 0·002 mole) in 20 cc chloroform was heated under reflux for 1 hr with evolution of hydrogen chloride. After heating the solution with excess ethanol to remove chloroform, a viscous product separated, and solidified on standing, wt 0·65 g (yield 57%). Crystallization from several solvents was unsuccessful, the dichloride separating as an amorphous white solid, m.p. 95–120°. (Found: Te, 22·44; Calc. for $C_{23}H_{25}O_2Cl_3Te$: Te, 22·49%).

2,2-*Diphenyl*-5-(p-*ethoxyphenyl-diiodotellurium*)-4-*pentanolactone* (XI). A mixture of 2,2-diphenyl-5-(*p*-ethoxyphenyl-dichlorotellurium)-4-pentanolactone (0·57 g; 0·001 mole), and a solution of sodium bisulphite was maintained at normal temp for 48 hr. The yellow oil formed was extracted with pet ether (50–70°), the solution evaporated, the oily residue dissolved in benzene and treated with a benzene solution of an equimolar quantity of iodine and the crude diiodide precipitated by addition of pet ether (50–70°), wt 0·70 g (yield 93%). The product crystallized from chloroform and pet ether (50–70°) in reddish needles m.p. 187–188° (dec). (Found: Te, 17·02; Calc. for $C_{25}H_{24}O_3I_2Te$: Te, 16·92%).

By reduction with hydrated solium sulphide at 100°, di-(*p*-ethoxyphenyl)-ditelluride m.p. 107°[4] was formed.

The same diiodide was obtained by treating an acetone solution of the corresponding dichloride with potassium iodide.

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