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ORGANIC TELLURIUM COMPOUNDS—IV

VINYLIC AND ETHYNYLIC TELLURIUM DERIVATIVES

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Abstract—The reaction of tellurium tetrachloride with phenyl- and diphenyl-acetylene yields vinyltellurium trichlorides. 2-Naphthyl-(2-phenylvinyl) telluride was obtained by the reaction of 2-naphthyltellurenyl iodide with β-styryl magnesium bromide. Acetylenic derivatives of tellurium were prepared starting from phenylethynyl magnesium bromide.

In this series, the addition of tellurium tetrachloride and aryltellurium halides to simple and activated double bonds has been studied.[1] This research has now been extended to the formation of vinyltellurium derivatives by addition to triple bonds.

It is shown that tellurium tetrachloride reacts with acetylenic compounds giving rise to substituted β-chlorovinyltellurium trichlorides (II).

$$TeCl_4 + \underset{I}{C_6H_5—C{\equiv}C—R} \rightarrow \underset{II}{C_6H_5—CCl{=}CR—TeCl_3}$$

a: $R = H$
b: $R = C_6H_5$

As Ib is symmetrical only one product (II) can be formed. The configuration of the latter was not considered since the stereochemistry of the addition to triple bonds is not much studied and gives rise to both *cis* and *trans* isomers.[2]

However, in the case of Ia two isomers are theoretically possible. By analogy with the addition of hydrobromic acid,[3] water,[4] hypohalogen acid,[5] methyl hypochlorite[6] and phosphorous pentachloride[7] to phenylacetylene, in which the positive fragment adds to the β carbon, it has been assumed that IIa has the phenyl group attached in the β position. A theoretical consideration supporting this orientation is the decreased dipole moment of *p*-nitrophenylacetylene in relation to nitrobenzene.[8]

The 2-chloro-2-phenylvinyltellurium trichloride has a peculiar property, not observed in other trichlorides, of being transformed into a mixture of tellurium tetrachloride and di-(2-chloro-2-phenylvinyl)tellurium dichloride (III) when treated with hydroxylated solvents:

$$\underset{IIa}{2C_6H_5CCl{=}CHTeCl_3} \rightarrow TeCl_4 + \underset{III}{(C_6H_5CCl{=}CH)_2TeCl_2}$$

However, due to hydrolysis the tellurium tetrachloride was not isolated. It must

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[1] M. de Moura Campos and N. Petragnani, *Tetrahedron Letters* 6, 11 (1959); M. de Moura Campos and N. Petragnani, *Chem. Ber.* **93**, 317 (1960).

[2] G. W. Wheland, *Advanced organic Chemistry* p. 406. John Wiley, London (1960).

[3] J. N. Nef, *Liebigs Ann.* **308**, 264 (1899).

[4] C. Friedel and M. Balsohn, *Bull. Soc. Chim. Fr.* (2) **35**, 54 (0000).

[5] N. Whittorf, *J. Russ. Phys. Chem. Ges.* **32**, 88, 117; *Chem. Zentr.* 1900 II, 29.

[6] E. J. Jackson, *J. Amer. Chem. Soc.* **56**, 977 (1934).

[7] E. Bergmann and A. Bondi, *Chem. Ber.* **66**, 278 (1933).

[8] P. W. Robertson, W. E. Dasent, R. M. Milburn and W. H. Olivier, *J. Chem. Soc.* 1628 (1950).

be pointed out that the dichloride (III) could not be formed from the direct reaction of tellurium tetrachloride with excess of phenylacetylene.

The reduction of the trichloride (IIb) lead to the formation of the expected ditelluride (IV) while IIa decomposed into elementary tellurium:

$$2\text{IIb} \xrightarrow{\text{red}} \underset{\text{IV}}{(C_6H_5\text{—}CCl\text{=}CC_6H_5)_2Te_2}$$

The dichloride (III) behaves normally in the reduction giving rise to the telluride (V). Addition of iodine to the latter produced the corresponding diiodide (VI) also formed by the reaction of III with potassium iodide.

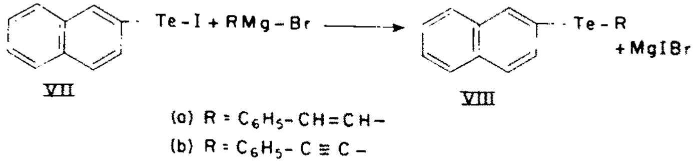
$$\text{III} \xrightarrow{\text{red}} \underset{\text{V}}{(C_6H_5CCl\text{=}CH)_2Te}$$

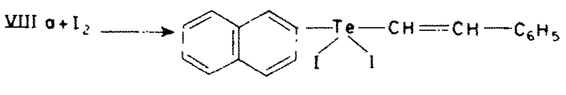
$$\text{V} + I_2 \rightarrow \underset{\text{VI}}{(C_6H_5CCl\text{=}CH)_2TeI_2} \leftarrow I^- + \text{III}$$

Attempts to add bromine to the double bond of the trichlorides (II) were unsuccessful. An unexpected reaction occurs, tellurium being removed from the organic compound as tellurium tetrabromide.

p-Ethoxyphenyltellurium trichloride does not react with phenyl- and diphenylacetylene. This is in accordance with the known decreased activity of aryltellurium trichlorides as compared with tellurium tetrachloride.[1]

Application of the Vicentini method[9] for the preparation of mixed tellurides by reaction of 2-naphthyltellurenyl iodide (VII) with β-styryl magnesium bromide resulted in another vinyltellurium derivative (VIIIa). This same reaction with phenylethynyl magnesium bromide produced the corresponding acetylenic telluride (VIIIb).





IX

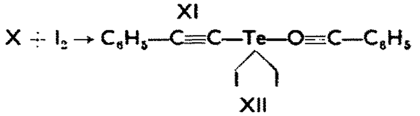
Compounds of this type have not been described in the literature. The compound VIIIa due to difficulty of purification was isolated as the corresponding diiodide (IX).

A diacetylenic telluride was formed and isolated as the diiodide (XII) by application of the Rheinboldt and Petragnani reaction[10] to phenylethynyl magnesium bromide.

$$4C_6H_5\text{—}C\equiv C\text{—}Mg\text{—}Br + TeCl_4 \rightarrow \underset{\text{X}}{C_6H_5\text{—}C\equiv C\text{—}Te\text{—}C\equiv C\text{—}C_6H_5} + 4MgClBr$$

$$\vdots$$

$$\underset{\text{XI}}{C_6H_5\text{—}C\equiv C\text{—}C\equiv C\text{—}C_6H_5}$$



$$\text{X} + I_2 \rightarrow C_6H_5\text{—}C\equiv C\text{—}\underset{I\;\;I}{Te}\text{—}O\equiv C\text{—}C_6H_5$$

XII

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[9] G. Vincentini, E. Giesbrecht, and L. R. M. Pitombo, *Chem. Ber.* **92**, 40 (1959).

[10] H. Reinboldt and N. Petragnani, *Chem. Ber.* **89**, 1270 (1956).

Although the total yield of this reaction was low (33 per cent) due to the formation of an unidentified amorphous by-product,* the diphenyldiacetylene (XI) anticipated in the reaction, was isolated in the corresponding equimolar quantities.

An attempt to obtain di-(β-styryl)telluride employing this reaction, resulted in a mixture of unidentified tellurium compounds.

EXPERIMENTAL

2-chloro-2-phenylvinyltellurium trichloride (IIa). Tellurium tetrachloride (2·70 g, 0·010 mole) was triturated in a mortar with a solution of phenylacetylene (1·20 g; 0·010 mole + 15%) in 10 cc carbon tetrachloride. A yellow solution formed with evolution of heat and immediate separation of the yellow trichloride, yield 3·50 g (94%), crystallizing from benzene in yellow prisms, m.p. 205–215° (dec) (Found: Te, 34·54; Calc. for $C_8H_6Cl_4Te$: Te, 34·34%). By using a large excess of phenylacetylene (1:4) the same trichloride was obtained in 79% yield.

Di-(2-chloro-2-phenylvinyl)tellurium dichloride (III). A yellow solution of 2-chloro-2-phenylvinyltellurium trichloride (1·50 g; 0·004 mole) in glacial acetic acid was heated a few minutes until decolourized. On cooling, the dichloride precipitated as colourless needles, yield 0·80 g (83%) and recrystallized from glacial acetic acid in colourless needles m.p. 205–215° (dec) (Found: Te, 27·19; Calc. for $C_{16}H_{12}Cl_4Te$: Te, 26·94%). The same result was obtained by using ethanol instead of glacial acetic acid. The acetic filtrate from the dichloride, after heating a few minutes in an open vessel, yielded hydrolysis products of tellurium tetrachloride as an inorganic white amorphous mixture infusible and soluble in conc sulphuric acid giving a colourless solution. The tellurium analysis agreed with a mixture of tellurium dioxide and tellurium oxychloride (Found: Te, 66·3; Calc. for TeO_2: Te,79·9%; Calc. for $TeOCl_2$: Te, 59·4%).

Reduction of 2-chloro-2-phenylvinyltellurium trichloride. The trichloride when treated with excess of hydrated sodium sulphide of sodium bisulphite is decomposed into elementary tellurium.

Di-(2-chloro-2-phenylvinyl)telluride (V). Di-(2-chloro-2-phenylvinyl)tellurium dichloride (0·80 g; 0·0017 mole) was added to 7 g hydrated sodium sulphide ($Na_2S{\cdot}9H_2O$) and the mixture heated at 100° for 15 min. The telluride separated as a red oil which solidified on addition of water, yield: 0·68 g (100%), and crystallized from ethanol orange yellow needles, m.p. 59–61° (Found: Te, 31·83; Calc. for $C_{16}H_{12}Cl_2Te$: Te, 31·68%).

Di-(2-chloro-2-phenylvinyl)tellurium diiodide (VI). A suspension of di-(2-chloro-2-phenylvinyl)-tellurium dichloride (0·55 g; 0·0012 mole) in a small volume of ethanol was treated with excess aqueous potassium iodide. The crude diiodide was washed with aqueous potassium iodide, yield: 0·75 g (98%) and crystallized as red brilliant crystals from benzene and pet ether (50–70°) m.p. 168–169° (dec). (Found: Te, 19·60; Calc. for $C_{16}H_{12}Cl_2I_2Te$: Te, 19·43%).

The same diiodide was obtained in quantitative yield by treating a benzene solution of di-(2-chloro-2-phenylvinyl)telluride with an equimolar amount of iodine in benzene and addition of excess pet ether (50–70°). A mixed m.p. with the diiodide prepared from the dichloride was not depressed.

2-chloro-1,2-diphenylvinyltellurium trichloride (IIb). A mixture of tellurium tetrachloride (1·35 g; 0·005 mole) and diphenylacetylene (1·00 g; 0·0055 mole) was refluxed in 20 cc carbon tetrachloride for 2 hr. The resulting yellow solution was evaporated leaving a yellow oil which crystallized, yield 1·70 g (77%). Two recrystallizations from glacial acetic acid furnished yellow prisms, m.p. 125–128°. (Found: Te, 28·85; Calc. for $C_{14}H_{20}Cl_4Te$: Te, 28·50%).

Di-(2-chloro-1,2-diphenylvinyl)ditelluride (IV). 2-chloro-1,2-diphenylvinyltellurium trichloride (1·35 g; 0·003 mole) was treated with 11 g hydrated sodium sulphide at 100° for 10 min. The ditelluride obtained as a dark paste crystallized by addition of water, yield; 1·02 g (100%) and recrystallized in orange needles from pet ether (50–70°), m.p. 151–152°. (Found: Te, 37·69; Calc. for $C_{28}H_{20}Cl_2Te_2$: Te, 37·38%).

Reaction of the trichlorides (II) *with bromine.* A benzene solution of 2-chloro-2-phenylvinyltellurium trichloride treated with bromine at room temp, gave rise to an orange precipitate. Under the same conditions, the 2-chloro-1,2-diphenylvinyltellurium trichloride was unreactive, tellurium tetrabromide being formed only after several hours heating under reflux. The tellurium tetrabromide gave a colourless solution in conc sulphuric acid, was influsible at 300^{c} and sublimed at 320°/2 mm Hg.

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* Probably formed by a mixture of compounds X, XI and addition products of type III.

Attempted reaction of p-*ethoxyphenyltellurium trichloride with phenyl- and diphenyl-acetylene.* *p*-Ethoxyphenyltellurium trichloride (0·36 g; 0·001 mole) was added, to a solution of phenylacetylene (2·00; 0·02 mole) in 15 cc chloroform, and the mixture refluxed for several hours. By concentration and addition of pet ether (50–70°) the trichloride was recovered unchanged.

In the same manner, starting with the diphenylacetylene analogue negative results were obtained.

2-naphthyl-(2-phenylvinyl)tellurium diiodide (IX). To a suspension of 2-naphthyltellurenyl iodide (1·80 g; 0·005 mole) in 15 cc dry benzene, *β*-styryl magnesium bromide (1·80 g; 0·009 mole) in 22 cc benzene–ether* was added.

A colourless solution with heat evolution was obtained and treated with aqueous ammonium chloride. The organic layer was dried (Na_2SO_4), evaporated and the residual oil solidified by addition of methanol, yield; 1·80 g. The product, an impure telluride, m.p. 80–95° was crystallized from methanol. A benzene solution of this impure product treated with the calculated amount of iodine in benzene, produced the corresponding diiodide (yield 59% referring to the tellurenyl iodide) which recrystallized from benzene and pet ether (50–70°) as brown greenish needles, m.p. 153–154° (dec) (Found: Te, 21·03; Calc. for $C_{18}H_{14}I_2Te$: Te, 20·86%).

2-naphtyl-phenylethynyltelluride (VIIIb). Reaction of 2-naphthyltellurenyl iodide (0·90 g; 0·0025 mole) with phenylethyl magnesium bromide (1·03 g; 0·005 mole) in 8 cc benzene–ether accordingy to the previous experiment, yielded the telluride, 0·85 g (95%). Crystallization from methanol furnished yellowish plates m.p. 88–89°. (Found: Te, 35·97; Calc. for $C_{18}H_{12}Te$: Te, 35·85%).

Di-(phenylethynyl)tellurium diiodide (XII). To a three necked round-bottom flask, fitted with a separatory funnel, a liquid sealed mechanical stirrer, a reflux condenser protected with a calcium chloride tube and an inlet tube, and containing a solution of tellurium tetrachloride (1·35 g; 0·005 mole in 50 cc dry ether, a solution of phenylethynylmagnesium bromide† (5·00 g; 0·025 mole) in 40 cc benzene–ether was added dropwise, bubbling nitrogen (free from oxygen) through the ice cooled reaction mixture. During this procedure an orange soft precipitate was formed. The heterogeneous mixture was refluxed for 1 hr and then 150 cc pet ether (50–70°) added. The solid was removed by filtration and washed with pet ether. It gave a positive test for magnesium and tellurium, but no definite compound could be isolated.

The orange organic solution was treated with aqueous ammonium chloride, dried (Na_2SO_4), and evaporated. The residual reddish oil dissolved in a small volume of benzene was treated with iodine (1·27 g; 0·005 mole) in benzene. A brown precipitate of the diiodide was formed by addition of pet ether, yield; 0·95 g; (33%) and recrystallized from benzene–pet ether in red needles, m.p. 120–125° (dec). (Found: Te, 21·98; Calc. for $C_{16}H_{10}I_2Te$; Te, 21·86%).

By evaporation of the mother liquor the crystalline diphenyldiacetylene separated, yield; 0·32 g (32%) and was recrystallized from dilethanol m.p. 85°.[13]

A similar reaction performed with *β*-styryl magnesium bromide produced no definite tellurium derivative, 1,4-diphenylbutadiene-1,3 being isolated.

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* This reagent was prepared in etheric solution according to Gilman and co-workers.[11] The resulting solution was diluted with equal volume of benzene.

† Prepared according to Kroeger and Niewland.[12]

[11] H. Gilman, E. A. Zoellner, W. M. Selby and C. Boatner, *Rec. Trav. Chim.* **54,** 584 (1935).

[12] J. W. Kroeger and J. A. Niewland, *J. Amer. Chem. Soc.* **58,** 1862 (1936).

[13] J. S. Salkind and F. B. Fundyler, *Chem. Ber.* **69,** 128 (1936).