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# ORGANIC TELLURIUM COMPOUNDS—VIII

## DI-ARYL TELLURIDES AS DEHALOGENATION AGENTS*—THE REDUCTION OF METALLIC SALTS BY DI-*p*-TOLYL TELLURIDE

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**Abstract**—The reaction of di-*p*-tolyltelluride with ferric, cupric and mercuric chloride, performed in glacial acetic acid, effects the reduction of the metallic salts giving rise to di-*p*-tolyltellurium dichloride. In toluene solution only the ferric chloride was reduced and the anhydride of di-*p*-tolyltellurium hydroxychloride formed, due to the hydrolysis of the tellurium dichloride. The reaction of the mentioned telluride and benzoyl chloride gave rise to a mixture of the dichloride and the dibenzoate. The mechanism of this reaction is discussed.

IN AN earlier communication[1] di-aryl tellurides were used as debromination agents, effecting the transformation of *vic*-dibromides in the corresponding olefins giving rise to di-aryl tellurium dibromides:

$$\text{Ar—Te-Ar} + \text{RCHBr-CHR'Br} \rightarrow \text{RCH=CHR'} + \text{Ar}_2\text{TeBr}_2$$

These results and the well-known halogenation of di-aryl tellurides[2] suggest us to extend this reaction to the field of the metallic halides.

$$\text{a Ar}_2\text{Te} + \text{b MeX}_n \rightarrow \text{a Ar}_2\text{TeX}_2 + \text{b MeX}_{n-2a}$$

The above reaction was performed by heating in a sealed tube equivalent amounts of di-*p*-tolyl telluride and the metallic salt in glacial acetic acid.

In this work, ferric, cupric and mercuric chloride were reduced to the lower chlorides, as shown in Table 1.

Under the same conditions, silver chloride was reduced in very small amounts. From the reaction mixture, great quantity of the starting materials were recovered unchanged.

Using toluene as solvent, the yields of the reduction of ferric chloride were lower, and the anhydride of the di-*p*-tolyl tellurium hydroxy chloride was obtained due to the hydrolysis of the corresponding dichloride, promoted by the presence of water.

$$2\text{FeCl}_3 + \text{Ar}_2\text{Te} \rightarrow 2\text{FeCl}_2 + \text{Ar}_2\text{TeCl}_2 \tag{1}$$

$$\text{Ar}_2\text{TeCl}_2 + \text{H}_2\text{O} \rightarrow \text{Ar}_2\text{Te(OH)Cl} + \text{HCl} \tag{2}$$

$$2\text{Ar}_2\text{Te(OH)Cl} \rightarrow \text{H}_2\text{O} + \text{Ar}_2\text{Te(Cl)—O—Te(Cl)Ar}_2 \tag{3}$$

$$\text{Ar} = p\text{-tolyl}$$

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[1] M. de Moura Campos, N. Petragnani and C. Thomé, *Tetrahedron Letters*, No. 15, 5 (1960).

[2] K. Lederer, *Ber. Dtsch. Chem. Ges.* **49**, 334 (1916); H. Rheinboldt and G. Vicentini, *Chem. Ber.* **89**, 624 (1956).

TABLE 1. REDUCTION OF METALLIC CHLORIDES BY DI-*p*-TOLYL TELLURIDE IN GLACIAL ACETIC ACID

| Starting material in moles | | Condition | | Me | Yield in % | |
|---|---|---|---|---|---|---|
| Telluride | Me $Cl_n$ | Temp | Time, in hr | | Tellurium dichloride | Me $Cl_{n-2a}$ |
| 0·005 | 0·01 | 100° | 10 | | 83 | 83 |
| | | + | | Fe | | |
| | | 140° | 1 | | | |
| 0·003 | 0·006 | 100° | 3½ | Cu | 83 | 100 |
| | | + | | | | |
| | | 140° | ¾ | | | |
| 0·0015 | 0·003 | 100° | 2 | Hg | 52 | 35 |
| | | + | | | | |
| | | 150° | 22 | | | |

In the absence of water the reactions (2) and (3) do not proceed, the di-*p*-tolyl tellurium dichloride being the only tellurium compound obtained.

Furthermore, the addition to the reaction mixture of small amounts of water increases the yield of the mentioned anhydride. The identity of the latter compound was readily established by elementary analysis, reduction to the corresponding telluride[3] and comparison with the known substance.[4]

It is interesting to point out that the reverse reaction can be carried out by stannous chloride,[5] being frequently used to effect the reduction of di-aryl tellurium dihalides.

$$SnCl_2 + Ar_2TeX_2 \rightarrow Ar_2Te + SnCl_2X_2$$

The reaction of ferric sulphate with di-*p*-tolyl telluride in glacial acetic acid promoted the reduction to ferrous sulphate in 73% yield, but not even one crystalline tellurium compound could be isolated from the reaction mixture, the principal product being elementary tellurium. On the other hand cupric sulphate was not reduced under the same experimental conditions.

Since *vic*-dibromides and allyl bromide[1] are easily transformed in olefins and hexadien-(1,5) during the reaction with tellurides, the transformation of benzoyl chloride into benzil was attempted, according to the equation:

$$2C_6H_5COCl + (p\text{-}CH_3\text{-}C_6H_4)_2Te \rightarrow (C_6H_5CO)_2 + (p\text{-}CH_3\text{-}C_6H_4)_2TeCl_2$$

However, the formation of benzil was never observed. The isolated crystalline products were di-*p*-tolyl tellurium dichloride, and in a relatively lower yield di-*p*-tolyl tellurium dibenzoate.

The structure of the latter compounds was established by:

(a) elementary analysis

(b) reduction to the initial telluride:

$$(p\text{-}CH_3C_6H_4)_2Te(OOC{-}C_6H_5)_2 \xrightarrow[100^\circ]{Na_2S\cdot 9H_2O} (p\text{-}CH_3C_6H_4)_2Te$$

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[3] L. Rheichel and E. Kirschbaum, *Ber. Dtsch. Chem. Ges.* **76**, 1105 (1934).

[4] K. Lederer, *Ber. Dtsch. Chem. Ges.* **47**, 277 (1914).

[5] E. Krause and G. Renwanz, *Ber. Dtsch. Chem. Ges.* **62**, 1714 (1929); *Ibid.* **65**, 782 (1932).

(c) a new synthesis starting from the organic tellurium dichloride and silver benzoate:

$$(p\text{-}CH_3C_6H_4)_2TeCl_2 + 2AgOOC{-}C_6H_5 \rightarrow 2AgCl + (p\text{-}CH_3C_6H_4)_2Te(OOC{-}C_6H_5)_2$$

The absence of benzil and the presence of the dibenzoate can be explained by the following sequence of reactions:

$$\begin{array}{ll} 2C_6H_5COCl + 2H_2O \rightarrow 2HCl + 2C_6H_5CO_2H & (1) \\ 2HCl + Ar_2Te + \frac{1}{2}O_2 \rightarrow H_2O + Ar_2TeCl_2 & (2) \\ 2C_6H_5CO_2H + Ar_2Te + \frac{1}{2}O_2 \rightarrow H_2O + Ar_2Te(C_6H_5CO_2)_2 & (3) \\ \hline 2C_6H_5COCl + 2Ar_2Te + O_2 \rightarrow Ar_2TeCl_2 + Ar_2Te(C_6H_5CO_2)_2 & \end{array}$$

The evidence of the proposed sequence can be taken from the following facts:

(1) Lederer[6] has shown, and we have confirmed, that tellurides can be easily transformed into the corresponding dichloride by the action of hydrochloric acid (35% yield). In the absence of oxygen the telluride was recovered unchanged.

(2) The dibenzoate was also prepared by us through step 3 (4% yield);

(3) Only small amounts of water are necessary to hydrolyse all the benzoyl chloride since water is reformed during steps 2 and 3;

(4) The reaction does not proceed when performed under nitrogen, the starting materials being recovered;

(5) The higher yield of the dichloride compared with the yield of the dibenzoate is consistent with the yield reported in 1 and 2.

The reported reaction of di-*p*-tolyl telluride with benzoyl chloride is being extended to other tellurides and acyl halides in order to see if, in some of these cases, a α-diketone can be obtained.

The mentioned reaction for the synthesis of the dibenzoate was extended to other dicarboxylates.

Only few compounds of this type are described in the literature. Vernon[7] and Lowry *et al.*[8] prepared some of this compound starting with silver salts, whereas Drew[9] and Balfe *et al.*[10] employed peracids or acyl peroxides as oxidant agents. Recently Prasad and Khaldelwal[11] have prepared tellurium tetracarboxylates through the reaction of tellurium tetrachloride and carboxylic acids in benzene solution.

The present paper reports the preparation of some di-*p*-tolyl tellurium dicarboxylates using the silver salt procedure.

$$Ar_2TeCl_2 + 2AgO_2C{-}R \rightarrow 2AgCl + Ar_2Te(O_2C{-}R)_2$$
$$Ar = p\text{-}CH_3\text{-}C_6H_4;\ R = C_3H_7,\ C_7H_{15},\ C_{11}H_{23}$$

When R was $C_5H_{11}$ and $C_9H_{19}$ a possible di-*p*-tolyl tellurium hydroxymonocarboxylate was formed. The structure of this compound and the general properties of the dicarboxylates are under investigation.

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[6] K. Lederer, *Liebig's Ann.* **391**, 326 (1912).

[7] R. H. Vernon, *J. Chem. Soc.* **117**, 86 (1920).

[8] T. M. Lowry and F. Huther, *Rec.* **55**, 688 (1936); T. M. Lowry and M. G. Ter Horst, *Rec.* **55**, 697 (1956).

[9] H. D. Drew, *J. Chem. Soc.* 3069 (1926).

[10] M. P. Balfe, C. A. Chaplin and H. Phillis, *J. Chem. Soc.* 346 (1938); M. P. Balfe and K. N. Nandi, *Ibid.*, 71 (1941).

[11] S. Prasad and B. L. Khandelwal, *J. Indian Chem. Soc.* **39**, 671 (1962).

## EXPERIMENTAL

*Reaction of ferric, cupric and mercuric chlorides with di-*p*-tolyl telluride in glacial acetic acid.* A mixture of di-*p*-tolyl telluride (1·62 g; 0·005 mole), $FeCl_3$ (1·62 g; 0·01 mole) and 2 ml glacial acetic acid was heated in a sealed tube at 100° for 10 hr and thereafter at 140° for 1 hr. The reacted mixture was treated with water, and the crystalline residue separated and washed with pet. ether giving rise to di-*p*-tolyl tellurium dichloride, wt 1·65 g; m.p. 170–172° (83% yield). The aqueous solution was titrated with $K_2Cr_2O_7$ showing a 83% reduction of the $FeCl_3$.

In the same manner, a mixture of di-*p*-tolyl telluride (1·00 g; 0·003 moles), $CuCl_2$ (0·87 g; 0·006 mole) and 4 ml glacial acetic acid gave rise to the equivalent amount of CuCl and di-*p*-tolyl tellurium dichloride (m.p. = 160–172°; 83% yield).

The reduction of $HgCl_2$ was performed in the same way giving rise to HgCl (35% yield), and the expected dichloride (52% yield).

*Reaction of silver chloride with di-*p*-tolyl telluride in glacial acetic acid.* A mixture of di-*p*-tolyl telluride (0·93 g; 0·003 mole), AgCl (0·86 g; 0·006 mole) and 75 ml glacial acetic acid was heated in a sealed tube at 160° during 168 hr. The solid residue obtained, wt 1·51 g, was treated with hot benzene, and afterwards with conc. $NH_4OH$ aq, giving rise to 0·04 g elementary Ag. From the $NH_4OH$ solution, after being treated with $HNO_3$ aq, AgCl wt 0·71 g (83% yield) was recovered. From the organic solution a great quantity of the starting telluride was recovered unchanged.

*Reaction of ferric chloride with di-*p*-tolyl telluride in toluene.* Equivalent amounts of di-*p*-tolyl telluride and $FeCl_3$ in toluene were refluxed during several hr. The insoluble residue was separated by filtration, washed with hot toluene and the $FeCl_3$ content determined. The organic solutions were evaporated, the residue washed with pet. ether to separate the unchanged telluride, and submitted to a fractional crystallization with a toluene–pet. ether mixture. Different amounts of di-*p*-tolyl tellurium dichloride (m.p. 168–172°) and the anhydride of di-*p*-tolyl tellurium hydroxy chloride (m.p. 260–265°) were obtained. (Found: Te, 36·28. Calc. for $C_{28}H_{28}Cl_2Te_2O$: Te, 36·11%). Table 2 summarizes the results obtained. The reduction of the anhydride with hydrated $Na_2S$ gave rise to the starting telluride (m.p. 65–66°).

Table 2. Reaction of ferric chloride with di-*p*-tolyl telluride in toluene

| Starting material | | | Time hr | Products obtained in % | | |
|---|---|---|---|---|---|---|
| Telluride in moles | Ferric chloride moles | Toluene in ml | | $FeCl_3$ | Dichloride | Anhydride |
| 0·003 | 0·006* | 50 | 5 | 42·5 | — | 25·2 |
| 0·005 | 0·010* | 100 | 5 | 53·0 | 46·7 | 10·6 |
| 0·001 | 0·002† | 20 | 1 | *a* | 90·0 | — |
| 0·0015 | 0·003† | 25‡ | 1 | *a* | 22·0 | 49·4 |

[a] not detected

* $FeCl_3 \cdot 6H_2O$

† p.a. grade anhydrous

‡ 5·8 g water added

*Reaction of ferric sulphate and cupric sulphate with di-*p*-tolyl telluride.* A mixture of di-*p*-tolyl telluride (0·62 g; 0·002 mole), $Fe_2(SO_4)_3$ (1·1 g; 0·002 mole) and 10 ml glacial acetic acid was heated at 150° during 6 hr. After 2 hr the formation of elementary Te was observed. The solid residue was separated by filtration and washed several times with water, giving rise to elementary Te. The ferrous salt content in the water solution was determined with dichromate (73% yield). The acetic acid solution was evaporated *in vacuo* giving rise to a black pasty residue. Attempts to isolate an organic Te compound from this residue were unsuccessful.

In a similar manner, from a mixture of di-*p*-tolyl telluride (0·62 g; 0·002 mole), hydrated $CuSO_4$ (1·00 g; 0·004 mole) and 4 ml glacial acetic acid, the starting materials were recovered unchanged.

*Reaction of di-*p*-tolyl telluride with benzoyl chloride.* A mixture of di-*p*-tolyl telluride (3·1 g;

0·01 mole) and benzoyl chloride (1·4 g; 0·01 mole) was heated at 150–160° over a period of 7 hr, in an apparatus protected against moisture. The dark pasty residue was treated with benzene giving rise to small amounts of elementary Te. The solution was evaporated and from the solid residue, by repeated fractional crystallization, di-*p*-tolyl tellurium dichloride, wt 1·64 g (86% yield) and di-*p*-tolyl tellurium dibenzoate, wt 1·27 g (46% yield) were obtained. The dibenzoate was recrystallized from a mixture of benzene and pet. ether (30–50°) giving rise to colourless needles, m.p. 232–235°. (Found: Te, 23·11. Calc. for $C_{28}H_{24}O_4Te$: Te, 23·08%).

Similar results were obtained with two equivalents of benzoyl chloride. The reaction did not take place when the above experiment was performed under nitrogen.

*Di-*p*-tolyl tellurium dibenzoate.* A mixture of di-*p*-tolyl tellurium dichloride (1·00 g; 0·025 mole) and silver benzoate (1·22 g; 0·053 mole), using an apparatus protected against moisture and light, in 25 ml purified dioxane, was refluxed 4 hr. The solid residue was washed with hot benzene giving rise to Ag salts, wt 0·66 g. The organic solutions were evaporated giving rise to crude dibenzoate, wt 1·39 g (96% yield). Recrystallization of a mixture of benzene and pet. ether produced colourless needles, m.p. 230–238°. Reduction with hydrated $Na_2S$ gave di-*p*-tolyl telluride, m.p. 63–65°.

*Di-*p*-tolyl dicarboxylates.* The dibutyrate, m.p. 125–127° (recrystallized from pet. ether 30–50°; (Found: Te, 25·97. Calc. for $C_{22}H_{28}O_4Te$: Te, 26·37%), the dicaprilate, m.p. 85–86° from methanol (Found: Te, 21·30%. Calc. for $C_{30}H_{44}TeO_4$: Te, 21·4%) and the dilaurate, m.p. 66–68° from ethanol (Found: Te, 17·86%. Calc. for $C_{38}H_{60}O_4Te$: Te, 17·99%), were prepared in a similar way.

In the case of the caproate and caprate, a probable di-*p*-tolyl tellurium hydroxymonocarboxylate was obtained. In the latter case, colourless needles formed, m.p. 136–137° (Found; Te, 28·8%. Calc. for $C_{20}H_{28}O_3Te$: Te, 28·87%) and in the former case colourless needles, m.p. 96–99°. (Found: Te, 26·3%. Calc. for $C_{24}H_{34}O_3Te$: Te, 25·58%).

*Di-*p*-tolyl tellurium dichloride.* To a solution of di-*p*-tolyl telluride (0·62 g; 0·002 mole) in 20 ml acetone 1 ml conc. HCl aq was added. After refluxing 12 hr, the solvent was evaporated giving rise to a solid residue, wt 0·81 g. Treating with pet. ether the insoluble di-*p*-tolyl tellurium dichloride was isolated, wt 0·26 g (m.p. 166–169°; 35% yield). From the pet. ether solution the starting telluride was recovered unchanged, wt 0·35 g. Furthermore, performing the reaction under $N_2$ the telluride was completely recovered.

*Reaction of di-*p*-tolyl telluride with benzoic acid.* A solution of di-*p*-tolyl telluride (0·61 g; 0·002 mole) and benzoic acid (0·48 g; 0·004 mole) in 20 ml acetone was refluxed 12 hr. The solid obtained after evaporation of the solvent was treated with 10% $NaHCO_3$ aq. The residue, wt 0·66 g, was treated with ethanol giving the insoluble dibenzoate, wt 0·045 g (m.p. 233–236°; 4·1% yield). From the alcoholic solution the starting telluride was recovered, wt 0·60 g, m.p. 61–65°.

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