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HALOGENODETELLURATION OF ARYLTELLURIUM(IV) COMPOUNDS

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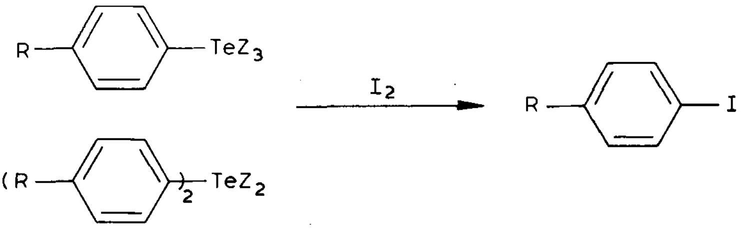
Summary

Some aryltellurium(IV) compounds react with iodine and bromine to give the corresponding aryl halides in good to moderate yields (iodo- and bromodetelluration). The addition of ammonium, cesium or potassium fluoride, antimony(V) chloride, and mercury(II) chloride accelerates the reaction in some cases. Compared to these halogenodetellurations, chlorodetelluration and cyanodetelluration of these compounds were very sluggish when various chlorinating agents and metal cyanides were used under several reaction conditions.

Many organotellurium compounds can be easily prepared [1] and yet their utility in organic synthesis seems to be limited to date [2—5]. We have been investigating the substitution of the tellurium moiety of organotellurium compounds by several functional groups [6—9] and have now found that the tellurium moiety of some easily accessible aryltellurium(IV) compounds can be replaced by halogen and cyanide to give the corresponding aryl halides and aryl cyanides, although the yield is not so satisfactory in some case [10]. It is known that the treatment of diorganyl tellurides (R_2Te) with halogens gives the corresponding stable organotellurium(IV) compounds (R_2TeX_2) (X = Cl, Br, I) [1]. Usually no carbon—tellurium bond fission occurs in such reactions, the cases of benzyl- [11] and vinyltellurium(IV) [6] compounds and 2-chloropropyltellurium trichloride [12] being exceptions. In the case of aryltellurium compounds only one example seems to have been reported; namely, the reaction of bis(2,2'-biphenylene)tellurium with bromine or iodine afforded the corresponding telluronium compounds where one C—Te bond was transferred to C—X bond (X = Br or I) [13]. There are no reports on the substitution of a tellurium moiety with cyanide or cyanogen.

Treatment of *p*-anisyltellurium trichloride with two equivalents of iodine in acetonitrile at reflux for 5 h afforded *p*-iodoanisole in a yield of 13%; *o*- and *m*-isomers and di-iodoanisole were not formed. Addition of potassium, cesium



or ammonium fluoride improved the product yield to 85%. The addition of mercury(II) chloride or antimony(V) chloride as catalysts also accelerated the reaction. *p*-Tolyltellurium trichloride similarly gave only *p*-tolyl iodide. These reactions did not proceed at all when potassium iodide was used instead of iodine. Similar treatment of diaryltellurium dichlorides afforded the corresponding aryl iodide in a lower yield. On the other hand, the reactions of phenyl- and *p*-bromophenyltellurium chlorides with iodine gave very low yields of the corresponding aryl iodides, even in the presence of metal or ammonium fluoride. These facts suggest the electrophilic nature of the reaction as in the cases of various halogenodemetallations, such as bromodeboronation, bromodesilylation, and iododestannylation [14]. The inorganic substituent (Cl, OAc, OCOCF$_3$) on tellurium did not affect the yield of aryl iodide. Typical results are summarized in Table 1. The addition of fluoride anion (to form ArTeCl$_3$F$_2$$^{2-}$, Ar$_2$TeCl$_2F_2$$^{2-}$) may increase the electron density on tellurium and consequently on the C—Te bond so as to make an electrophilic attack of halogen on it easier [15]. The role of the metal chloride seems to be the activation of iodine by complexation or the in situ formation of more reactive iodine mono-

TABLE 1

IODODETELLURATION OF ARYLTELLURIUM COMPOUNDS WITH IODINE

Te compound (mmol)		I$_2$ (mmol)	Additives (mmol)		Solvent (20 ml)	Reaction temp. (°C)	Reaction time (h)	Yield (%) [a] of ArI
p-MeOC$_6$H$_4$TeCl$_3$	2	4	—		MeCN	82	5	13
p-MeOC$_6$H$_4$TeCl$_3$	2	4	KF	4	MeCN	82	5	37
p-MeOC$_6$H$_4$TeCl$_3$	2	4	NH$_4$F	4	MeCN	82	5	39
p-MeOC$_6$H$_4$TeCl$_3$	2	4	NH$_4$F	4	MeCN	82	18	64
p-MeOC$_6$H$_4$TeCl$_3$	1	4	NH$_4$F	4	MeCN	82	5	85
p-MeOC$_6$H$_4$TeCl$_3$	1	4	CsF	4	MeCN	82	4	59
p-MeOC$_6$H$_4$TeCl$_3$	1	4	HgCl$_2$	1	MeCN	82	5	52
p-MeOC$_6$H$_4$TeCl$_3$	1	2	SbCl$_5$	1	CH$_2$Cl$_2$	40	5	57
p-MeOC$_6$H$_4$TeCl$_3$	2	4	—		DMF	90	5	21
p-MeOC$_6$H$_4$TeCl$_3$	2	4	—		1,4-Dioxane	101	5	9
(*p*-MeOC$_6$H$_4$)$_2$TeCl$_2$	1	4	KF	4	MeCN [b]	82	5	23
(*p*-MeOC$_6$H$_4$)$_2$Te(OAc)$_2$	1	4	KF	4	MeCN [b]	82	5	24
p-MeC$_6$H$_4$TeCl$_3$	1	4	—		MeCN	82	5	trace
p-MeC$_6$H$_4$TeCl$_3$	1	4	NH$_4$F	4	MeCN	82	5	46
PhTeCl$_3$	2	4	—		MeCN	82	5	trace
Ph$_2$TeCl$_2$	1	4	CsF	4	MeCN	82	5	4
Ph$_2$Te(OAc)$_2$	1	4	KF	4	MeCN	82	5	2
Ph$_2$Te(OCOCF$_3$)$_2$	0.5	2	KF	2	MeCN	82	5	1
Ph$_2$TeCl$_2$	1	4	Pd(OAc)$_2$	0.1	MeCN	82	5	4

[a] Determined by GLC; 1 mole of ArTeCl$_3$ corresponds to 1 mole of ArI, and 1 mole of Ar$_2$TeCl$_2$ to 2 mole of ArI. [b] MeCN (10 ml).

chloride [16]. The addition of a catalytic amount of palladium(II) salt did not improve greatly the yield of iodobenzene, although Te—Pd transmetallation was expected to occur to give phenylpalladium species [7] which may react with iodine to give a good yield of iodobenzene.

Treatment of *p*-anisyltellurium trichloride or di-*p*-anisyltellurium dichloride with bromine in acetonitrile, 1,4-dioxane, or CCl_4 afforded 2,4-dibromoanisole in a moderate to good yield, together with a small amount of the expected *p*-bromoanisole. In separate experiments it was found that *p*-bromoanisole can be readily brominated to 2,4-dibromoanisole in acetonitrile in the presence of tellurium tetrachloride. This fact shows that tellurium(IV) species functions as catalyst for a further bromination of *p*-bromoanisole under the present reaction conditions. Bromodetelluration of phenyl-, 2-naphthyl-, and *p*-bromophenyltellurium compounds was sluggish as in the case of iododetelluration, again suggesting an electrophilic nature of the reaction. In these cases even the addition of ammonium or cesium fluoride did not improve the product yield significantly. No bromodetelluration occurred in the reaction of aryltellurium trichloride with copper(I) or -(II) bromide in 1,4-dioxane.

Attempted chlorodetelluration of aryltellurium chlorides with various chlorinating agents such as molecular chlorine, antimony(V) chloride, t-butyl hypochlorite in CCl_4, acetonitrile or 1,4-dioxane resulted in the formation of only a low yield of the expected aryl chloride even from *p*-anisyltellurium trichloride [17]. Typical results of bromo- and chlorodetelluration are summarized in Table 2.

We have also tried cyanodetelluration of several aryltellurium compounds by treatment with various metal cyanides. As a result, a low yield (at most 8%) of aryl cyanide was obtained in the reaction using copper(I) cyanide [18] and *N,N*-dimethylformamide (DMF) as a solvent at a rather high temperature. Typi-

TABLE 2

BROMO- AND CHLORODETELLURATION OF ARYLTELLURIUM COMPOUNDS

Te compound (mmol)		Halogenating agent (mmol)		Solvent (ml)		Reaction temp. (°C)	Reaction time (h)	Product and Yield (%)[a]	
								ArX	ArX_2
$p\text{-}MeOC_6H_4TeCl_3$	1	Br_2	4	MeCN	20	82	3	1	85
$p\text{-}MeOC_6H_4TeCl_3$	2	Br_2	4	MeCN	20	35—45	20	trace	70
$p\text{-}MeOC_6H_4TeCl_3$	10	Br_2	20	1,4-Dioxane	10	10—15	20	trace	49
$p\text{-}MeOC_6H_4TeCl_3$	2	Br_2	4	CCl_4	20	30—40	20	trace	37
$(p\text{-}MeOC_6H_4)_2TeCl_2$	1	Br_2	4	MeCN	20	40—45	20	trace	76
$p\text{-}MeC_6H_4TeCl_3$	1	Br_2	4	MeCN	20	40	20	3	trace
$p\text{-}MeC_6H_4TeCl_3$	1	Br_2 [b]	4	MeCN	20	82	3	5	trace
$PhTeCl_3$	1	Br_2	2	MeCN	10	30—40	20	2	0
Ph_2TeCl_2	1	Br_2	4	MeCN	20	50—60	20	3	0
$Ph_2Te(OCOCF_3)_2$	0.5	Br_2 [c]	2	MeCN	10	82	3	trace	0
$p\text{-}MeOC_6H_4TeCl_3$	2	Cl_2	100	CCl_4	20	35—40	1.5	0	trace
$p\text{-}MeOC_6H_4TeCl_3$	1	$SbCl_5$	2	CCl_4	20	76	5	trace	4
$p\text{-}MeOC_6H_4TeCl_3$	1	t-BuOCl	2	MeCN	5	82	1	5	2
$p\text{-}MeOC_6H_4TeCl_3$	1	t-BuOCl	1	1,4-Dioxane	5	101	3	1	0

[a] Determined by GLC. See a footnote of Table 1. [b] NH_4F(4 mmol) was added. [c] NH_4F(2 mmol) was added.

TABLE 3

CYANODETELLURATION OF ARYLTELLURIUM COMPOUNDS WITH COPPER(I) CYANIDE

Te compound (mmol)		CuCN (mmol)	Solvent (ml)		Reaction temp. (°C)	Reaction time (h)	Yield (%)[a] of ArCN
Ph_2TeCl_2	2	4	DMF	25	160	3	8
Ph_2TeCl_2	1	2	DMF	10	160	5	6
$Ph_2Te(OCOCF_3)_2$	1	2	DMF	10	170	3	7
Ph_2TeCl_2	1	10	NMP[b]	5	150	5	4
Ph_2TeCl_2	1	10	HMPA[c]	7	150	5	2
p-$MeOC_6H_4TeCl_3$	1	10	DMF	5	160	5	1
(p-$MeOC_6H_4)_2Te(OCOCF_3)_2$	1	2	DMF	10	160	3	3
(p-$MeOC_6H_4)_2Te(OAc)_2$	1	2	DMF	10	160	3	2
(p-$BrC_6H_4)_2TeCl_2$	1	2	DMF	20	160	3	2

[a] Determined by GLC. See footnote of Table 1. [b] *N*-Methylpyrrolidone. [c] Hexamethylphosphoric triamide.

cal results are shown in Table 3. No aryl cyanide was obtained from the reaction with copper(II), silver(I), or potassium cyanide in methanol, acetonitrile, or DMF at various temperatures and even under UV irradiation.

Experimental

^1H NMR spectra were recorded with a Varian EM-360 (60 MHz) spectrometer in $CDCl_3$ or CCl_4. GLC analyses were carried out using a Shimadzu 4CMPF apparatus using EGSS-X(15%)—Chromosorb-W (1 or 3 m), Apiezon-L(25%)—Shimalite (1 m), and Silicone QF-1(30%)—Chromosorb-W (1 m) columns (N_2 as carrier gas). Commercially available organic and inorganic compounds were used without further purification. Aryltellurium trichlorides and diaryltellurium dichlorides were prepared as reported previously [7]. Di-*p*-anisyltellurium diacetate and bis(trifluoroacetate) were prepared by the reaction of Ar_2TeCl_2 with AgOAc in 1,4-dioxane [19] and with Ag_2O and trifluoroacetic acid in benzene [20], respectively; (p-$MeOC_6H_4)_2Te(OAc)_2$, m.p. 133—135°C (lit. [19] m.p. 135°C), $Ph_2Te(OCOCF_3)_2$, m.p. 96—98°C, (p-$MeOC_6H_4)_2Te(OCOCF_3)_2$, m.p. 100—103°C. Typical experimental procedures are given below.

Reaction of p-anisyltellurium trichloride with iodine in the presence of ammonium fluoride

A mixture of *p*-anisyltellurium trichloride (0.34 g, 1 mmol), iodine (1.01 g, 4 mmol), and ammonium fluoride (0.15 g, 4 mmol) in acetonitrile (20 ml) was stirred at reflux for 5 h. After the mixture had been cooled to room temperature, it was treated with aqueous NaCl (200 ml) and extracted with benzene (3 × 50 ml). The extracts were washed with $Na_2S_2O_3$ (aq. 10%) and then with aqueous NaCl and dried over Na_2SO_4. GLC analysis using *p*-iodotoluene as internal standard showed the presence of *p*-iodoanisole (0.85 mmol; 85%).

Reaction of di-p-anisyltellurium dichloride with iodine

A mixture of di-*p*-anisyltellurium dichloride (0.412 g, 1 mmol), iodine (1.02 g, 4 mmol), and potassium fluoride (0.232 g, 4 mmol) in acetonitrile (10 ml) was heated at reflux for 5 h. GLC analysis of benzene extract after the workup described above showed the presence of *p*-iodoanisole (0.46 mmol; 23%) and di-*p*-anisyl telluride (0.77 mmol; 77%) (*p*-iodotoluene and diphenyl telluride as internal standards for the former and the latter, respectively). The latter compound was produced by reduction of unreacted starting dichloride with $Na_2S_2O_3$.

Reaction of p-anisyltellurium trichloride with bromine

A mixture of *p*-anisyltellurium trichloride (0.68 g, 2 mmol) and bromine (0.64 g, 4 mmol) in acetonitrile (20 ml) was stirred at 35—45° C for 20 h. After the workup of the red-brown, homogeneous solution as described above, GLC analysis of the extracts using ethyl cinnamate as internal standard showed the presence of 2,4-dibromoanisole (1.39 mmol, 69.5%) and a trace amount of *p*-bromoanisole.

When a mixture of *p*-bromoanisole (ca. 9 mmol) and bromine (ca. 9 mmol) in CCl_4 or acetonitrile (20 ml) was stirred at room temperature for 5 h in the presence of tellurium tetrachloride (1 mmol), 75% of *p*-bromoanisole was converted to 2,4-dibromoanisole (by GLC determination). Similar treatment without $TeCl_4$ afforded only ca. 5% yield of 2,4-dibromoanisole.

Reaction of diphenyltellurium bis(trifluoroacetate) with copper(I) cyanide

A stirred mixture of diphenyltellurium bis(trifluoroacetate) (0.51 g, 1 mmol) and copper(I) cyanide (0.18 g, 2 mmol) in DMF (10 ml) was heated at 165—175° C for 3 h. After the green homogeneous mixture had cooled to room temperature, it was treated with aqueous NaCl (250 ml) and the precipitated white grey solid was filtered and the filtrate extracted with benzene (3 × 50 ml). The extracts were washed with aqueous $Na_2S_2O_3$ and then with aqueous NaCl and dried over Na_2SO_4. GLC analysis of the extracts using *p*-tolyl cyanide as internal standard revealed the presence of benzonitrile (0.14 mmol, 7%) and diphenyl telluride (0.16 mmol, 16%).

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