

## Reactions of Diaryltellurides with Some Organic Halides & Sn(IV) Tetraiodide : Electrophilic Cleavage of Te-Allyl Bond

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Diaryltellurides,  $R\text{Te}R'$  ( $R=R' = \text{C}_6\text{H}_5$ , or  $p\text{-CH}_3\text{OC}_6\text{H}_4$ ; and  $R = \text{C}_6\text{H}_5$ ,  $R' = p\text{-CH}_3\text{OC}_6\text{H}_4$ ) react with allyl bromide, cyclohexyl iodide,  $\text{CH}_2\text{I}$ ,  $\text{C}_6\text{H}_5\text{X}$  ( $\text{X} = \text{Br}, \text{I}$ ) or  $\text{SnI}_4$  to give corresponding triorganotelluronium halides. The Te-allyl bond is readily cleaved by electrophiles such as  $\text{Br}_2$ ,  $\text{I}_2$ ,  $\text{ICl}$ ,  $\text{BrCN}$ ,  $\text{ICN}$ .

ALKYL halides have been known to add to diorganotellurides to give telluronium salts<sup>1</sup>. It has been established that the aromatic tellurides are less reactive than the corresponding aliphatic derivatives and for alkyl halides, in general, reactivity decreases in the series,  $\text{RI} \gg \text{RBr} > \text{RCl}$ . The reaction of aromatic halides with diorganotellurides does not appear to have received serious attention and the reaction of  $(\text{CH}_3)_2\text{Te}$  (prepared *in situ*) with  $\text{C}_6\text{H}_5\text{I}$  appears to be the only reported reaction of an aryl halide<sup>2</sup>.

Although cleavage of Te-aryl<sup>3,4</sup>, Te-benzyl<sup>5</sup> and Te-C (in ylids)<sup>6</sup> by electrophiles has been recently reported, there appears to be no report of the similar cleavage of Te-allyl or Te-vinyl compounds.

We report in this paper the results of investigation on (i) addition of allyl bromide, phenyl bromide (or iodide), cyclohexyl iodide or methyl iodide to diaryltellurides, (ii) fission of Te-allyl bond with electrophiles, (iii) insertion of  $\text{Ar}_2\text{Te}$  between Sn-I bond and (iv) attempted preparation of an unsymmetric tetraorganotellurium(IV) derivative.

### Materials and Methods

Diphenyltelluride<sup>7</sup> and bis(*p*-methoxyphenyl)telluride<sup>8</sup> were prepared by reported methods. Phenyl (*p*-methoxyphenyl)tellurium dichloride was prepared by a modified method. Phenyltellurium trichloride and anisole were heated (145-60°) for ~ 6 hr. The dichloride crystallized out on the addition of ether. It was recrystallized from acetonitrile. Phenyl (*p*-methoxyphenyl)telluride was obtained by the reduction of the dichloride with hydrated sodium sulphide.

Some typical reaction of diphenyltelluride, bis(*p*-methoxyphenyl)telluride, phenyl (*p*-methoxyphenyl)telluride with organic halides are described and the characterization data of the products obtained are given in Tables 1 and 2.

(a) *Reaction of phenyl(p-methoxyphenyl)telluride with methyl iodide* —  $\text{C}_6\text{H}_5(p\text{-CH}_3\text{OC}_6\text{H}_4)\text{Te(II)}$  (1.5 g, 4 mmol) dissolved in methyl iodide (3 ml) was allowed to stand for 48 hr, ether added and the crystalline solid obtained was stored in ether

for ~ 12 hr before filtration. Reactions of cyclohexyl iodide was similarly carried out (Table 1).

(b) *Reaction of diphenyltelluride with allyl bromide* — Diphenyltelluride (1.13 g, 4 mmol) dissolved in allyl bromide (5 ml) was heated at ~70° for 40 hr and allowed to stand overnight. The colourless crystals which separated on the addition of ether were filtered after keeping them in ether for 24 hr.

(c) *Reaction of bis(p-methoxyphenyl)telluride with tin tetraiodide* — The solution of tin tetraiodide (1.87 g, 3 mmol) in benzene (50 ml) was slowly added to a stirred solution of bis(*p*-methoxyphenyl)telluride (1.023 g, 3 mmol). The mixture was stirred for 5 hr and then kept overnight. Reddish brown crystals of  $\text{R}_2\text{TeSnI}_4$  were filtered and dried.

(d) *Cleavage of allyldiphenyltelluronium bromide by iodine* — To a stirred solution of allyldiphenyltelluronium bromide (4.02 g, 10 mmol) in chloroform (50 ml) was added dropwise, a solution of iodine (2.54 g, 10 mmol) in the same solvent (30 ml). The violet colour of iodine disappeared immediately after each addition. On evaporation of solvent, reddish brown crystals of  $(\text{C}_6\text{H}_5)_2\text{TeIBr}$  separated out, filtered and washed with ether; yield 4 g (85%), m.p. 210° (212-13)°. The filtrate on evaporation of the solvent gave allyl iodide, yield 1.34 g (80%), b.p. 102° (102°/744 mm).

### Results and Discussion

Allyl bromide has been previously reported<sup>10</sup> to form  $\text{Ph}_2\text{TeBr}_2$  and  $(\text{CH}_2=\text{CH}-\text{CH}_2)_2$  when heated with diphenyltelluride at 180° for 3 hr. We have however, found that diaryltellurides when stirred in refluxing allyl bromide (b.p. 70°) for 40 hr, yield allyldiaryltelluronium bromides in >90% yield.

The reactions of cyclohexyl iodide with  $\text{R}_2\text{Te}$  (alkyl or aryl), which have not been observed before, proceed normally. (The compounds containing unsubstituted cyclohexyl group bonded to tellurium have not been reported previously).

Unlike, alkyl halides, reactions with aryl halides are sluggish. Phenyl bromide or iodide reacts with

TABLE 1 — ANALYTICAL DATA OF ORGANOTELLURIUM DERIVATIVES OBTAINED BY THE EQUATION :  $R_2Te + XY \rightarrow R_2TeXY$ 

Products (*) RR'TeXY		m.p. (°C)	Yield %	Found (calc.) (%)			
X	Y			Te	X	C	H
$R = R' = C_6H_5$							
Br	Allyl <sup>(b)</sup>	130	94	31.50 (31.67)	20.35 (19.83)	43.69 (44.72)	3.80 (3.75)
I	Cyclohex.	192-94	100	25.98 (25.94)	25.79 (25.80)	43.80 (43.95)	4.32 (4.30)
I	C <sub>6</sub> H <sub>5</sub>	247 (247-48) <sup>15</sup>	65	—	—	—	—
Br	C <sub>6</sub> H <sub>5</sub>	>248 (260) <sup>16</sup>	45	—	—	—	—
SnI <sub>2</sub>	I	220	100	—	54.02 (55.89)	15.92 (15.87)	0.99 (1.10) <sup>(c)</sup>
$R = R' = p-CH_3OC_6H_4$							
Br	Allyl	126-28	93	27.89 (27.56)	17.29 (17.26)	44.10 (44.11)	4.29 (4.13)
I	Cyclohex.	178	92	23.10 (23.11)	22.84 (22.99)	43.91 (43.52)	4.52 (4.56)
I	C <sub>6</sub> H <sub>5</sub>	208 (210) <sup>17</sup>	60	—	—	—	—
Br	C <sub>6</sub> H <sub>5</sub>	84-86	38	21.30 <sup>(e)</sup> (25.57)	12.99 (16.01)	—	—
SnI <sub>2</sub>	I	165	90	—	50.29 (52.43)	—	(e)
$R = C_6H_5; R' = p-CH_3OC_6H_4$							
I	CH <sub>3</sub>	55-56	94	28.11 (28.11)	27.94 (27.96)	37.44 (37.05)	3.12 (3.33)
Br	Allyl	170	97	29.35 (29.48)	18.14 (18.46)	44.35 (44.40)	3.00 (3.05)
I	Cyclohex.	135	94	23.80 (24.44)	24.30 (24.31)	43.78 (43.72)	4.84 (4.44)
SnI <sub>2</sub>	I	158-60	100	—	52.99 (54.10)	—	—

(\*) Cyclohexyl derivatives are reddish brown, other products are colourless.

(b) PMR : 87.56 (*m*, phenyl), 3.28-2.95 (*d*-CH<sub>2</sub>Te), 2.81-2.65 (*d*-CH<sub>2</sub>=C), 4.25-3.94 (*m*, CH protons)

(c) Compound impure

(d) Found : mol. wt 900.2, Reqd : 908.1

(e) Found : mol. wt 722.0. Reqd : 968.1

TABLE 2 — CLEAVAGE REACTIONS OF DIARYLALLYLTELLURONIUM BROMIDE BY ELECTROPHILES

Reactants (1:1) (RR' C <sub>6</sub> H <sub>5</sub> TeBr + XY)			Time (hr) and temp. (°C)	Products (RR'TeBrY)	m.p. (°C) (lit m.p.)	Yield %
R	R'	XY				
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	I <sub>2</sub>	4(25)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> TeIBr	210(210-13) <sup>9</sup>	85
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	IBr	4(0)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> TeBr <sub>2</sub>	200(203-4) <sup>4</sup>	65
C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	BrCN	8(25)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> TeBrCN	222(225) <sup>9</sup>	62
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	ICN	8(25)	( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> TeBrCN	228(230) <sup>9</sup>	78
<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	Br <sub>2</sub>	4(0)	( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> TeBr <sub>2</sub>	194(198) <sup>9</sup>	80
C <sub>6</sub> H <sub>5</sub>	<i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	IBr	4(0)	(C <sub>6</sub> H <sub>5</sub> ) ( <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> )-TeBr <sub>2</sub>	144(149) <sup>18</sup>	65

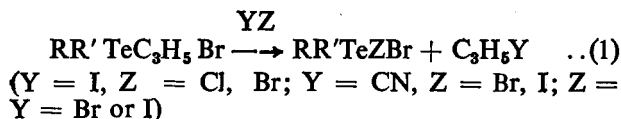
diaryl tellurides only when the reaction mixture is stirred (~ 50 hr) at 150°; corresponding triaryl-telluronium salts are obtained in moderate yield (65% when X = I and 40% when X = Br).

These telluronium halides are crystalline solids with sharp melting points. Conductances in acetonitrile and acetone are in the range 114 to 139 and from 105-125 Ω<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> respectively, thereby indicating their 1:1 electrolytic behaviour<sup>11</sup>. The molecular weights determined in freezing nitro-

benzene indicate that the compounds are dissociated in solution. Calculated values of van't Hoff factor is ~ 2.

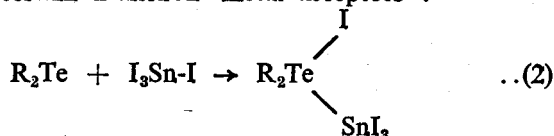
*Cleavage of Te-allyl bond*— We have recently observed<sup>12</sup> that Te-C bond (s) in (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub> TeCl<sub>2</sub> and telluracyclopentyl iodide are stable towards halogens and pseudohalogens, viz., Br<sub>2</sub>, I<sub>2</sub>, ICl, IBr or ICN. The Te-allyl bond however is readily cleaved in presence of electrophiles (XY) in accordance with Eq(1). Since aryl halides could not be

detected, it is inferred that Te-allyl bond is cleaved in preference to Te-aryl bond.



In order to prepare a tetraorganotellurium(IV) compound containing four different organic groups phenyl(*p*-methoxyphenyl)telluride was reacted with methyl iodide and the resulting telluronium salt isolated and then treated with cyclopentadienylthallium(CpTl). Thallous iodide separated out in quantitative yield, but the tellurium-containing product could not be characterized due to its ready decomposition: tetraalkyl and dialkyldiaryl-tellurium(IV) derivatives are in general unstable and have not yet been isolated<sup>13</sup>.

The reaction with SnI<sub>4</sub>(Eq. 2) is interesting as R<sub>2</sub>Te(II) usually acts as a Lewis base towards HgX<sub>2</sub> and certain transition metal acceptors<sup>14</sup>.



Our preference for the insertion products (Eq. 2) over 1:1 adducts R<sub>2</sub>Te → SnI<sub>4</sub> is based on the fact that the products are monomeric in freezing benzene and behave as 1:1 electrolytes in acetonitrile (in this respect these resemble triorganotellurium halides).

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### References

1. IRGOLIC, K. J., *J. organometal. Chem.*, **103** (1975), 91.
2. THAYER, J. S. & SMITH, K. V., *Syn. inorg. Metalorg. Chem.*, **3** (1973), 101.
3. HELLWINKEL, D. & FAHRBACH, G., *Ann. chem.*, **712** (1968), 1.
4. WITTIG, G. & FRITZ, H., *Ann. chem.*, **577** (1952), 39.
5. VICENTINI, G., *Chem. Ber.*, **91** (1958), 801.
6. SADEKOV, I. D., VSACHEV, V. I. & MINKIN, V. I., *Zh. obshch. Khim.*, **48** (1978), 475.
7. ADLOFT, M. & ADLOFT, J. P., *Bull. Soc. chim. Fr.*, (1966), 3304.
8. TANIYAMA, H., MIYOSHI, F., SAKAKIBARA, E. & UCHIDA, H., *Yakugaku zasshi*, **77** (1957), 191; *Chem. Abstr.*, **51** (1957), 10407i.
9. SRIVASTAVA, T. N., SRIVASTAVA, R. C. & MALA SINGH., *J. organometal Chem.*, **160** (1978), 449.
10. DE MOURA CAMPOS, M., PETRAGNANI, N. & THOME, C., *Tetrahedron Lett.*, **15** (1960), 5.
11. GREAY, W. J., *Coord. Chem. Rev.*, **7** (1971), 181.
12. SRIVASTAVA, T. N., SRIVASTAVA, R. C. & MALA SINGH., *Indian J. Chem.*, **17A** (1979), 615.
13. HELLWINKEL, D. & FAHRBACH, G., *Chem. Ber.*, **101** (1968), 574.
14. IRGOLIC, K. J. & ZINGARO, R. A., *Organometallic reactions*, Vol. 2 edited by E. Becker and M. Sutsui (Wiley Interscience, New York), 1971, 210.
15. LEDERER, K., *Chem. Ber.*, **44** (1911), 2287.
16. RHEINOLDT, H. & PETRAGNANI, N., *Chem. Ber.*, **84** (1956), 1270.
17. LEDERER, K., *Chem. Ber.*, **49** (1916), 1615.
18. RHEINOLDT, H. & VICENTINI, G., *Chem. Ber.*, **89** (1956), 624.