The Reaction of Organic Dihalides with Organyltelluride (RTe^-) Anions: Telluronium Salts and Charge-transfer Complexes†

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The reaction of NaTeR (R = p-EtOC$_6$H$_4$ or Ph) with organic dihalides $(CH_2)_nX_2$ (n = 1—4) affords telluronium salts (n = 3 or 4; X = Cl or Br) the nature of which is discussed. For n = 1 (X = Br or I) the products are formulated as charge-transfer complexes of stoicheiometry $(RTe)_2CH_2{\cdot}CH_2X_2$. For n = 2, elimination of ditelluride occurs with formation of an alkene. The compound NaTeR is shown to be an effective dehalogenating agent for *vic*-dihalides. Some ^{125}Te Mössbauer data are discussed and it is suggested that the unusually low value of Δ (7.58 mm s^{-1}) for $(p\text{-}EtOC_6H_4Te)_2CH_2{\cdot}CH_2Br_2$ relates to removal of 5p-electron density from the spare-pair orbital *via* the charge-transfer interaction. The related di-iodomethane complex gives a solid-state e.s.r. signal. Mass spectroscopic data are discussed and these support the formulations proposed.

The reaction of a diorganyl ditelluride (R_2Te_2) with aqueous alkaline sodium tetrahydroborate affords a solution with the chemical properties of NaTeR.[1] Our work had its origin in a desire to synthesise a range of bis(tellurides), $RTe(CH_2)_nTeR$, and to study the ligand chemistry of these potentially bidentate materials. It seemed that nucleophilic attack by RTe^- on organic dihalides, $X(CH_2)_nX$ (X = halogen, normally Br), would be worth examining; hence we carried out two-phase reactions (both in the presence and absence of a phase-transfer catalyst) involving NaTeR and the dihalides. Here we report on the products obtained.

The literature[2] contains a report of the synthesis of $(RTe)_2CH_2$ (R = p-MeOC$_6$H$_4$ or p-EtOC$_6$H$_4$) from the reaction of diazomethane with a ditelluride.

Experimental

(*a*) *Synthesis.*—Two methods of preparation were used. These are illustrated for the reaction of di(p-ethoxyphenyl) ditelluride[3] with 1,4-dibromobutane.

1-*Bromo*-1-p-*ethoxyphenyltelluracyclopentane. Method A.* Di(p-ethoxyphenyl) ditelluride (6.2 mmol) in benzene (2.5 cm^3) and ethanol (7.5 cm^3) was heated to reflux. To this solution, sodium tetrahydroborate (10 mmol) in 1 mol dm^{-3} sodium hydroxide (8.5 cm^3) was added dropwise. The reaction mixture became colourless on completion of the addition. 1,4-Dibromobutane (1 mmol) in benzene (5 cm^3) was then added, and the warm mixture was stirred for 30 min. A fibrous white precipitate was obtained in 80% yield which was filtered off, washed with diethyl ether, and dried *in vacuo*. Recrystallisation from acetonitrile gave a white material, m.p. 280 °C.

Method B. Di(p-ethoxyphenyl) ditelluride (1 mmol) in benzene (50 cm^3) was treated with a solution of NaBH$_4$ (10 mmol) and benzyltri-n-butylammonium bromide (2 mmol) in 1 mol dm^{-3} sodium hydroxide (20 cm^3). The mixture was stirred for 2 h during which time the colour of the ditelluride was lost. 1,4-Dibromobutane (1 mmol) was added and stirring continued for 4 h at room temperature. On setting aside, a fibrous precipitate was obtained in 70% yield and was separated, washed with diethyl ether, and dried *in vacuo*. Recrystallisation from acetonitrile gave the compound described in method A.

It was found that 1,4-dichlorobutane was effective in the above preparations. Generally method A was used with the following organic dihalides: CH_2Br_2, CH_2I_2, and $(CH_2)_3Br_2$. Reactions with dichloromethane gave products of indefinite composition containing tellurium–oxygen bonds (i.r.). Some reactions were also carried out using diphenyl ditelluride.[4]

Reactions with dihalogenoethanes. When method A was used with dibromomethane and NaTeR, evolution of ethene occurred with regeneration of R_2Te_2. 2,3-Dibromobutane gave but-2-ene (g.l.c.) and ditelluride; 2,3-dibromo-2-methylpentane gave 2-methylpent-2-ene (g.l.c.). 1,2-Dibromocyclohexane afforded cyclohexene (g.l.c., i.r.), and, interestingly, 2-iodo-2-methylbutane gave 2-methylbut-2-ene (g.l.c.).

(*b*) *Physical Measurements.*—Infrared spectra (4 000—250 cm^{-1}) were measured using a Perkin-Elmer 457 instrument, mass spectra with an AEI MS9 instrument (70 eV). G.l.c. analyses were carried out with Pye-Unicam equipment. Elemental analyses for carbon and hydrogen were obtained from the Microanalytical Service, Department of Chemistry, University of Aston. Conductivities were measured over a concentration range for aqueous solutions using a standard bridge.

Some ^{125}Te Mössbauer data were obtained at Simon Fraser University, Burnaby, Canada, at 4 K using equipment previously described.[5]

^{13}C N.m.r. spectra for p-EtOC$_6$H$_4$Te(CH$_2$)$_4$Br were obtained in dimethyl sulphoxide (dmso) and in water. A ^{125}Te n.m.r. spectrum for the same compound was obtained in dmso. The compound has only limited solubility and no ^{13}C–^{125}Te coupling was detectable in the ^{13}C spectrum. Proton n.m.r. spectra were measured in (CD$_3$)$_2$SO using either a Perkin-Elmer R14 or JEOL FX 90Q instrument. The ^{13}C and ^{125}Te n.m.r. data were obtained at the Université de Rouen as previously described.[6]

Analytical data are given in Table 1 and Mössbauer data in Table 2. Data for 1-chloro-1-p-ethoxyphenyltelluracyclopentane are compared in Table 3 with data for some telluronium salts derived from 1,3-dihydro-2-telluraindene which have previously been published. Several of these salts have been characterised crystallographically. The main features of the mass spectra are summarised in Schemes 1 and 2.

Discussion

Reaction with Dihalogenobutanes and Propanes.—The use of conventional phase-transfer catalysis was of no obvious

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† *Non. S.I. units employed:* eV ≈ 1.60 × 10^{-19} J, G = 10^{-4} T.

Table 1. Analytical data for new organotellurium compounds

	Analysis (%)					
	Found		Calculated			
Compound	C	H	C	H	Λ_M [a] (water)	M.p. (°C)
$[(p\text{-EtOC}_6H_4)Te]_2CH_2{\cdot}CH_2Br_2$ [b]	30.0	3.10	31.5	3.20	—	154
$[(p\text{-EtOC}_6H_4)Te]_2CH_2{\cdot}CH_2I_2$	27.2	2.90	27.8	2.80	—	118
$(p\text{-EtOC}_6H_4)Te(CH_2)_3Br$	36.0	3.80	35.5	4.00	—	260—262
$(p\text{-EtOC}_6H_4)Te(CH_2)_4Br$	37.2	4.40	37.4	4.40	176	258—260
$PhTe(CH_2)_4Br$	34.9	3.60	35.1	3.80	—	280
$(p\text{-EtOC}_6H_4)Te(CH_2)_4Cl$	41.9	5.10	42.3	4.90	185	228—230
$PhTe(CH_2)_4Cl$	39.9	4.10	40.4	4.35	—	240

[a] In ohm^{-1} cm^2 mol^{-1}; extrapolation to infinite dilution. [b] Te: found 37.7, calc. 37.2%, Br: found 24.1, calc. 23.4%.

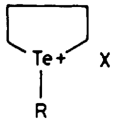
Table 2. ^{125}Te Mössbauer data (mm s^{-1}) for reaction products of $NaTe(C_6H_4OEt\text{-}p)$ with dibromoalkanes

Compound	δ [a]	Δ [b]	$\Gamma_{\frac{1}{2}}$
$[(p\text{-EtOC}_6H_4)Te]_2CH_2{\cdot}CH_2Br_2$	0.53	7.58	6.33
$(p\text{-EtOC}_6H_4)Te(CH_2)_3Br$	0.36	5.58	5.68
$(p\text{-EtOC}_6H_4)Te(CH_2)_4Br$	0.38	5.50	5.43

[a] ±0.08 mm s^{-1}, *vs.* $^{125}Sb/Cu$. [b] Quadrupole splitting (±0.1 mm s^{-1}).

advantage in reactions of 1,4-dichloro- or 1,4-dibromobutane with sodium organotellurates, NaTeR. However, we have previously shown that when the catalyst is supported on an expandable clay good yields of product may be obtained in a short time.[7]

The reaction of tetrahydroborate-reduced ditellurides, R_2Te_2, with $(CH_2)_nX_2$ (n = 3 or 4) gives materials of stoicheiometry $RTe(CH_2)_nX$. Our most extensive studies have been with the n = 4 compounds since these show potential for application to organic synthesis.[8] The compounds $RTe(CH_2)_4X$ (R = p-$EtOC_6H_4$ or Ph; X = Cl or Br) are salt like and dissociate as 1 : 1 electrolytes in water. ^{125}Te Mössbauer data for $(p\text{-EtOC}_6H_4)Te(CH_2)_4Br$ are typical of a tellurium(IV) compound and, in particular, Δ is in the expected range for a telluronium salt. Thus the most acceptable formulation of the product is as a telluronium salt derived from 1-telluracyclopentane (I). Nucleophilic attack on 1,4-dibromobutane by RTe^- has taken place, but quaternisation then proceeds more rapidly than attack at the second C–X bond by further RTe^-. (It seems likely that the telluronium salt may function as a phase-transfer catalyst once small quantities have been formed, thus helping to explain why no advantage accrues from the use of benzyltri-n-butylammonium bromide.)



(I)

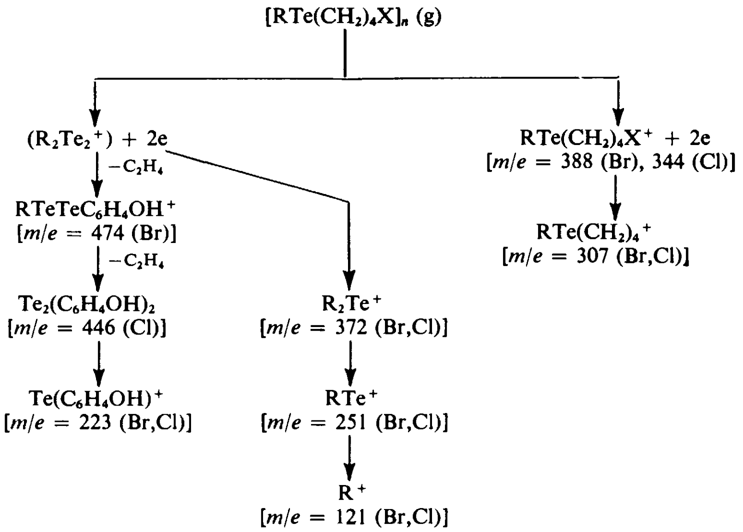
The mass spectra of $RTe(CH_2)_4X$ (X = Cl or Br) support formulation (I) and, in general respects, do not differ greatly from the spectra of a range of salts based on 1,3-dihydro-2-telluraindene.[6] In particular, the observation of fragments containing two tellurium atoms may reflect a degree of association in the solid state which is quite normal for this variety of compound.[9] The broad features of the spectra may be related as in Scheme 1.

Attempts were made to study the n.m.r. spectra of the products from the reaction of 1,4-dichlorobutane with $NaTe(C_6H_4OEt)$. The compound was not excessively soluble but a ^{13}C n.m.r. spectrum was obtained in dmso (Table 3) which was essentially the same as for a solution in D_2O, a solvent in which salt-like character has been demonstrated. Significant ion pairing occurs in dmso since Λ_M was 13.6 ohm^{-1} cm^2 mol^{-1} compared with values in excess of 30 ohm^{-1} cm^2 mol^{-1} expected for strong electrolytes. The spectrum is certainly inconsistent with an open-chain structure $RTe(CH_2)_4Cl$ for which extra carbon resonances would be expected, also it contains features in common with data for salts derived from 1,3-dihydro-2-telluraindene.[6,8] The ^{125}Te data are also consistent with the telluronium salt formulation since the chemical shift is within the range for similar compounds. We have previously demonstrated that $\delta(^{125}Te)$ is sensitive both to the anion and the quaternising group R within a given solvent for a particular series of telluronium salts.[6] Thus despite the limited solubility of the material, these n.m.r. data provide good support for the proposed structure (I).

The product of the reaction of $NaTe(C_6H_4OEt)$ with 1,3-dibromopropane is, from the Mössbauer data, also a telluronium salt. It seems improbable that it should be formulated as a derivative of 1-telluracyclobutane since such a ring would be too strained. Thus a polymeric formulation is more plausible and, indeed, the mass spectra of such compounds are very complex with many fragments of significantly higher m/e than $[RTe(CH_2)_3X]^+$.

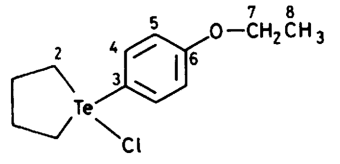
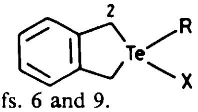
Reactions with Dihalogenomethanes.—The reaction of NaTeR with dibromo- or di-iodo-methane followed a different course. In this instance, nucleophilic substitution of both halogen atoms proceeds but the products are isolated as pale yellow (CH_2Br_2) or deep yellow (CH_2I_2) solids containing 1 mol of dihalogenomethane, $(RTe)_2CH_2{\cdot}CH_2X_2$ (X = Br or I). The mass spectra (Scheme 2) are in accord with this formulation. [Products from the reaction with CH_2Br_2 sometimes showed variable C analysis figures but this correlates with partial loss of dibromomethane. Preliminary experiments indicate that the materials behave as bis(telluride) ligands with ' soft ' metal centres.]

I.r. and ^1H n.m.r. spectra support the formulation of the complexes. For example strong features at 1 114, 725, and 592 cm^{-1} in the spectrum of $[(p\text{-EtOC}_6H_4)Te]_2CH_2{\cdot}CH_2I_2$ certainly arise from CH_2I_2 and correlate with bands at 1 100, 721, and 599 cm^{-1} in the free liquid. A rather dilute solution of $[(p\text{-EtOC}_6H_4)Te]_2CH_2{\cdot}CH_2I_2$ in $(CD_3)_2SO$ gave a ^1H n.m.r.



Scheme 1. Major peaks in the mass spectrum of $(p\text{-EtOC}_6H_4)\overline{Te(CH_2)_4}X$ (X = Cl or Br). Quoted *m/e* values are referenced to ^{130}Te, ^{37}Cl, ^{81}Br, ^{12}C, ^{1}H, and ^{16}O. A round bracket around a fragment implies not observed and (Br and/or Cl) implies observed for indicated X only

Table 3. Carbon-13 and ^{125}Te n.m.r. data for 1-telluracyclopentane derivatives in dmso

Compound	$\delta(^{13}C)$ *vs.* $SiMe_4$	$\delta(^{125}Te)$ *vs.* Me_2Te
	31.43 (C^1), 35.68 (C^2), ? (C^3), 134.66 (C^4), 115.73 (C^5), 160.11 (C^6), 63.21 (C^7), 14.33 (C^8)	761
	34.4 * (C^2) (R = Me, X = I) 34.3 * (C^2) (R = allyl, X = Br)	651 * (R = Me, X = I) 688.3 * (R = allyl, X = Br) 722 * (R = benzyl, X = Br)

* Data from refs. 6 and 9.

(*a*) $[(p\text{-EtOC}_6H_4)Te]_2CH_2{\cdot}CH_2I_2$

$[(p\text{-EtOC}_6H_4)Te]_2CH_2^+$,	$(p\text{-EtOC}_6H_4)_2Te_2^+$,	$(p\text{-EtOC}_6H_4)_2Te^+$,	$CH_2I_2^+$,	$(p\text{-EtOC}_6H_4)Te(CH_2)^+$,	$(p\text{-EtOC}_6H_4)Te^+$,	$(p\text{-HOC}_6H_4)Te^+$
(*m/e* = 516)	(*m/e* = 502)	(*m/e* = 372)	(*m/e* = 268)	(*m/e* = 265)	(*m/e* = 251)	(*m/e* = 223)

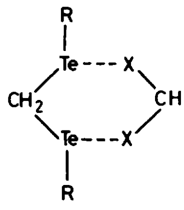
(*b*) $(PhTe)_2CH_2{\cdot}CH_2I_2$

$(PhTe)_2CH_2^+$,	$Ph_2Te_2^+$,	$Ph(CH_2)TeI^+$,	Ph_2Te^+,	$CH_2I_2^+$,	$PhTe^+$
(*m/e* = 428)	(*m/e* = 414)	(*m/e* = 348)	(*m/e* = 348)	(*m/e* = 268)	(*m/e* = 207)

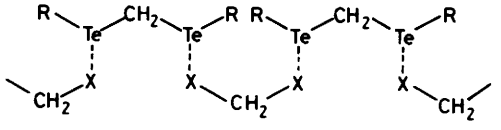
Scheme 2. Tellurium-containing fragments in mass spectra of charge-transfer complexes of $RTe(CH_2)TeR$ with di-iodomethane. Quoted *m/e* values are relative to ^{130}Te, ^{12}C, ^{1}H, ^{16}O and ^{127}I

spectrum in which significant broadening of signals had occurred, doubtless due to the paramagnetism detected by e.s.r. spectroscopy (see below); the spectrum integrates correctly but the broad lines mask coupling of the $Te{-}CH_2{-}Te$ methylene protons to ^{125}Te (natural abundance 6.99%).

A Mössbauer spectrum has been obtained for $[(p\text{-EtOC}_6H_4)Te]_2CH_2{\cdot}CH_2Br_2$ and it will be noted (Table 2) that the parameters are out of step with those of the telluronium salts discussed above. The chemical isomer shift is, within the errors, more positive than is δ for the other two compounds which implies a greater *s*-electron density at tellurium in this compound. This may imply that some mechanism is operative which leads to withdrawal of 5*p*-electron density thus deshielding the 5*s* pair. This hypothesis gains more positive support from the value of Δ which is significantly lower than that expected (*ca.* 10 mm s^{-1}) for a telluride.[5] At the same time the value is too high for a telluronium salt. We suggest that the material is a charge-transfer complex and two possible formulations are the illustrated (IIa) and (IIb). The compound $[(p\text{-EtOC}_6H_4)Te]_2CH_2{\cdot}CH_2I_2$ gives a broad e.s.r. signal in the solid state ($\Gamma_{\frac{1}{2}} \simeq 75$ G) centred on $g = 2.18$. The suggestion that these materials are indeed charge-transfer complexes is the only one which offers a self-consistent interpretation of all the data. It is proposed that electron density is transferred from the spare-pair *p* orbital on tellurium. This will decrease the *p*-orbital occupational im-



(IIa)



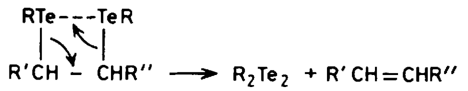
(IIb)

balance and, accordingly, reduce Δ. Simultaneously removal of *p*-electron density will increase δ. Similar effects have been noted for organotellurium complexes with 7,7,8,8-tetracyanoquinodimethane (tcnq)[10] and the implication is that the charge transfer is considerable.

We have previously suggested that a charge-transfer interaction may be the first step in the oxidative addition of methyl iodide to diphenyl telluride.[11] These data support that hypothesis.

Very recently, Engman and Cava[12] reported that the reaction of LiTeR with dichloromethane affords $RTeCH_2TeR$ (*e.g.* R = benzo[*b*]thien-2-yl).

Reactions with Dibromoethanes and other vic-*Dibromides.*—Only brief comment is necessary. Addition of these dibromides to the colourless solution of NaTeR produced the familiar ditelluride colouration and, indeed, R_2Te_2 was recovered quantitatively. The other product was (when dibromides were used) an alkene which was generally identified by g.l.c. Thus it is possible that the nucleophilic substitution proceeds and that ditelluride then eliminates in a concerted process (Scheme 3). It is of interest that 2-iodo-2-methylbutane gave 2-methylbut-2-ene under these conditions. We have not checked the generality of this reaction. It was recently shown that sodium hydrogentelluride was a useful debrominating agent,[13] it would appear that NaTeR is no less effective.



Scheme 3.

Acknowledgements

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References

1 J. L. Piette and M. Renson, *Bull. Soc. Chim. Belg.*, 1970, **79**, 353, 369, 383.
2 N. Petragnani and G. Schill, *Chem. Ber.*, 1970, **103**, 2271.
3 G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 1925, 2307.
4 J. L. Piette and M. Renson, *Bull. Soc. Chim. Fr.*, 1971, 925.
5 C. H. W. Jones, R. Schultz, W. R. McWhinnie, and N. S. Dance, *Can. J. Chem.*, 1976, **54**, 3234.
6 A. Z. Al-Rubaie, W. R. McWhinnie, P. Granger, and S. Chapelle, *J. Organomet. Chem.*, 1982, **234**, 287.
7 P. Monsef-Mirzai and W. R. McWhinnie, *Inorg. Chim. Acta*, 1981, **52**, 211.
8 A .Z. Al-Rubaie, Ph.D. Thesis, University of Aston in Birmingham, 1982.
9 R. H. Jones and T. A. Hamor, *J. Organomet. Chem.*, 1982, **234**, 299.
10 H. B. Singh, W. R. McWhinnie, R. F. Ziolo, and C. H. W. Jones, *J. Chem. Soc., Dalton Trans.*, submitted for publication.
11 N. S. Dance, W. R. McWhinnie, J. Mallaki, and Z. Monsef-Mirzai, *J. Organomet. Chem.*, 1980, **198**, 131.
12 L. Engman and M. P. Cava, *Organometallics*, 1982, **1**, 470.
13 K. Ramasamy, S. K. Kalyanasundaram, and P. Shanmugam, *Synthesis*, 1978, 311.

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