

SOLUTION STUDIES OF TRIORGANOTELLURONIUM SALTS

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Summary

Evidence for telluronium ylid formation via the salt method is obtained for $\text{Ph}_2\text{Te}(\text{CH}_2\text{COPh})\text{Br}$, but generally telluronium salts $(\text{aryl})_2\text{Te}(\text{CH}_2\text{R})\text{X}$ rapidly dissociate in chloroform solution to $(\text{aryl})_2\text{Te}$ and RCH_2X . The relative rates of dissociation of $\text{Ph}_2(\text{CH}_3)\text{TeX}$ in CHCl_3 are: $\text{X} = \text{I} > \text{Br} \sim \text{NCS} > \text{Cl} > \text{PhCOO}$. Conductivity and ^1H NMR data suggest the salts $\text{Ph}_2(\text{CH}_3)\text{TeX}$ to be covalent and at least dimeric in CHCl_3 , but more ionic in DMSO and, to a lesser extent, DMF. IR data indicate association in solid $\text{Ph}_2(\text{CH}_3)\text{TeI}$.

Kinetic data show that the reaction of CH_3I with excess Ph_2Te (solvent) affords an equilibrium mixture of ionic and covalent forms of $\text{Ph}_2(\text{CH}_3)\text{TeI}$, the ionic species being formed via the covalent one. Spin trapping experiments with phenyl(*t*-butyl)nitron indicate that oxidative addition of alkyl halides to Ph_2Te and reductive elimination of CH_3SCN from $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{NCS})$ proceed via radical pathways. A mechanism is proposed for oxidative addition which involves the preformation of a charge transfer complex of RX (alkyl halide) and diphenyltelluride.

Introduction

Our interest in telluronium salt chemistry originated some years ago when we decided to employ the salt method of ylid formation in an attempt to extend the range of telluronium ylids beyond the two then known [1,2]. We therefore synthesised a range of salts $\text{R}_2\text{Te}(\text{CH}_2\text{R}')\text{X}$ where R was aryl, R' was Ph or PhCO and X was halogen, generally Br or I . Although we did obtain in one experiment evidence for the synthesis of $\text{Ph}_2\text{Te}-(\text{CH}_2\text{COPh})$ (see Experimental section), our efforts were generally frustrated by the fact that, in several solvents, reductive elimination of $\text{R}'\text{CH}_2\text{X}$ occurred more rapidly than removal of HX by base. Extension of the series of salts, e.g. to $\text{R}' = \text{H}$, revealed that, in

solvents such as chloroform, reaction 1 was general.



We have now investigated the above reaction in some detail, and some interesting features have been uncovered. Some of our data for $X = \text{halogen}$ were initially difficult to interpret unambiguously, consequently we extended our series of anions X to thiocyanate [3] and benzoate. The restriction of R to Ph and of R' to H made for easier spectroscopic interpretation. We recently published data for $\text{Ph}_2\text{Te}(\text{CH}_3)(\text{NCS})$ [3]. This study showed that reductive elimination of (exclusively) methyl thiocyanate occurred in chloroform solution from a "covalent" form of the "salt". Kinetic data indicated that two pseudo-first order rate processes were involved, the second (faster) of which required the presence of Ph_2Te and this did not become dominant until a reasonable concentration of telluride built up. A further suggestion from the study was that, based on circumstantial evidence, a radical mechanism was involved.

In this paper we report our new data which we believe to be helpful in building up an understanding of these telluronium salt systems in solution. We also report spin trapping experiments which give further support for the involvement of radicals in both the forward and back reactions in 1.

Experimental and results

(a) Synthesis of telluronium salts

The salts used in this investigation were prepared by the indicated literature methods: $\text{Ph}_2\text{Te}(\text{CH}_3)\text{I}$, $\text{Ph}_2\text{Te}(\text{CH}_3)\text{Br}$, $\text{Ph}_2\text{Te}(\text{CH}_3)\text{Cl}$, $\text{Ph}_2\text{Te}(\text{CH}_3)(\text{NO}_3)$ [4]; Ph_3TeI , Ph_3TeBr , Ph_3TeCl [5]; $\text{Ph}_2\text{Te}(\text{CH}_2\text{Ph})\text{Br}$ [6]; $\text{Ph}_2\text{Te}(\text{CH}_2\text{COPh})\text{Br}$ [7]; $\text{Ph}_2\text{Te}(\text{CH}_3)(\text{NCS})$ [3]. All compounds gave satisfactory analysis and had melting points in good agreement with those reported in the literature.

Methyldiphenyltelluronium benzoate. Methyldiphenyltelluronium iodide (1 g, 0.002 mol) and silver benzoate (0.46 g, 0.002 mol) were added to distilled water (50 cm³) and the mixture was stirred for 30 min at room temperature. Subsequently the mixture was heated under reflux for 4 h. The precipitate of silver iodide was removed and weighed to confirm the quantitative nature of the reaction. The filtrate was concentrated and set aside during which period a white crystalline material formed. The product was collected and dried over P_4O_{10} to m.p. 105°C. (Found: C, 57.6; H, 4.40. Calculated for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{Te}$: C, 57.5; H, 4.34%).

The above reactions when carried out with silver acetate afforded the required amount of silver iodide but on work up only Ph_2Te was obtained. Clearly methyl acetate (b.p. 57°C) had been lost either via thermal decomposition of the salt or, more probably, by loss of the ester subsequent to reductive elimination.

The benzoate salt is soluble in methanol, chloroform, dimethylsulphoxide (DMSO) and dimethylformamide (DMF), but insoluble in benzene and carbon tetrachloride.

(b) Attempted synthesis of telluronium ylids

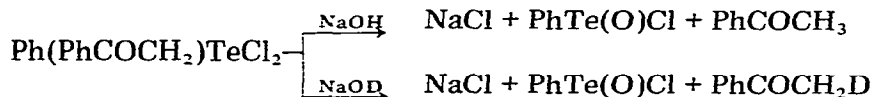
We report briefly on those experiments which initiated the work.

(i) *Experiments with diphenylbenzyl bromide.* Triethylamine (1 g, 0.01 mol) was dissolved in deuteriated chloroform (5 cm³) and diphenylbenzyltelluronium bromide (2.25 g, 0.005 mol) was added. The solution was shaken for 5 min and a ¹H NMR spectrum recorded. The spectrum showed the presence of Ph₂Te, N(C₂H₅)₃ and [(PhCH₂)N(C₂H₅)₃]⁺Br⁻. The experiment was repeated and the ¹H NMR spectrum was recorded immediately. A new resonance at δ = 4.45 ppm (vs TMS) was noted (PhCH₂Br), however this was rapidly replaced by a new resonance at δ = 4.80 ppm ([PhCH₂N(C₂H₅)₃]⁺). The telluronium salt alone when dissolved in CDCl₃ gives only the methyl resonance at δ = 4.45 ppm and the IR spectrum shows only the presence of PhCH₂Br and Ph₂Te.

(ii) *Experiments with diphenylphenacyltelluronium bromide.* Diphenylacyltelluronium bromide (2.40 g, 0.005 mol) was added to CDCl₃ (5 cm³) and treated with an excess of aqueous sodium hydroxide (1 M). The mixture was shaken for 2 min over which period in the white salt dissolved to afford a yellow chloroform layer. The chloroform was separated and, on setting aside, the solution deposited a white solid shown to be a quantitative yield of diphenyltellurium oxide, Ph₂TeO. The ¹H NMR spectrum of the filtrate showed only resonances due to PhCOCH₃ (δ(Me) = 260 ppm). The overall reaction was:



The reaction was repeated using NaOD/D₂O, the reaction was identical in all respects except that the methyl singlet at δ = 2.60 ppm was entirely absent, hence PhCOCD₃ had been formed. We then investigated the base hydrolysis of Ph(PhCOCH₂)TeCl₂ which was shown to proceed as follows:



Finally, diphenylphenacyltelluronium bromide was mixed with triethylamine in the presence of CDCl₃. Triethylammonium bromide (insoluble in chloroform) was formed and the ¹H NMR spectrum showed two new features of interest: (a) the aromatic proton resonances had shifted to lower field (compared with the spectrum when NaOH was used) implying that the aromatic groups were bonded to a more electropositive centre. (b) A new singlet at δ = 6.3 ppm was noted for which the aromatic : singlet ratio was 15 : 1. Removal of the solvent left an oil which deposited Ph₂TeO.

The design of the above experiments were dictated by the insolubility of Ph₂Te(CH₂COPh)Br in chloroform. However, when the chloroform soluble (p-CH₃OC₆H₄)₂Te(CH₂COPh)Br was used, immediate reductive elimination of PhCOCH₂Br occurred.

(c) Solution properties of telluronium salts

(i) *Conductivity data.* Conductivities were measured for a range of telluronium salts in both DMSO and DMF (see also ref. 3). DMF was dried over Linde 4A molecular sieves and distilled under reduced pressure. DMSO was dried over NaOH and distilled under reduced pressure. Measurements were made with a standard bridge and a Mullard type E7591 B cell (bright platinum electrodes). The conductivity of each salt was examined over a range of concentration and

TABLE 1

SINGLE CONCENTRATION ($10^{-3} M$) VALUES OF MOLAR CONDUCTIVITY (Λ_M) FOR TELLURONIUM SALTS ^a

Compound	Solvent/molar conductivity ($\text{ohm}^{-1} \text{cm}^{-1} \text{mol}^{-1}$)	
	DMF	DMSO
$\{(\text{C}_2\text{H}_5)_4\text{N}\}\text{Cl}$	80	30.0
$\text{Ph}_2(\text{CH}_3)\text{TeCl}$	40	11.0
$\text{Ph}_2(\text{CH}_3)\text{TeBr}$	29	13.5
$\text{Ph}_2(\text{CH}_3)\text{TeI}$	48	14.5
Ph_3TeCl	36	9.5
Ph_3TeBr	44	11.5
$\text{Ph}_2(\text{PhCH}_2)\text{TeBr}$	44	10.0
$\text{Ph}_2(\text{CH}_3)\text{Te}(\text{OOCPh})$	16	20.1

^a Each salt, in each solvent, gives non linear plots of Λ_M versus (concentration)^{1/2}.

plots of Λ vs. (conc)^{1/2} were made. In each case the plot showed considerable curvature indicating substantial ion pairing. Table 1 gives some single concentration ($10^{-3} M$) data for the two solvents.

(ii) *¹H NMR spectra of diphenylmethyltelluronium salts.* The ¹H NMR spectra were determined with a Varian Instruments HA 100 spectrometer (100 MHz) using TMS as internal reference. Some data were also obtained with a Perkin Elmer R12B instrument. The resonance of methyl groups bonded to tellurium were recognized by the presence of satellites arising from coupling to ¹²⁵Te ($J(^{125}\text{Te}-^1\text{H}) = 24-25\text{Hz}$). In DMSO-*d*₆ solution the spectra were invariant with time in all cases except one. With $\text{Ph}_2(\text{CH}_3)\text{TeI}$ a small trace of MeI was noted. ($\delta = 2.15$ ppm) but this remained constant, thus the equilibrium, which favoured the salt, was established very rapidly. With $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{OOCPh})$ a singlet at $\delta = 2.86$ ppm ($J = 24$ Hz) diminished over some days to be replaced by a new signal at $\delta = 3.85$ ppm (shown to be CH_3OOCPh).

In CDCl_3 the methyltelluronium salts all underwent decomposition:



In each case CH_3X was recognised by the ¹H NMR methyl resonance (comparison with authentic sample). Only one methyl-containing product was seen and the total methyl integrated intensity remained constant during the reactions, thus the stoichiometry is as presented in eq. 2. In the case of $\text{X} = \text{OOCPh}$ or Cl the reaction did not go to completion but reached equilibrium at approximately 50% decomposition. The relative rates of reductive elimination were:



Table 2 gathers some pertinent ¹H NMR data.

(iii) *Kinetic studies with diphenylmethyltelluronium iodide.* The chemical shifts for the methyl resonance of $\text{Ph}_2(\text{CH}_3)\text{TeI}$ in DMSO was markedly different from that in CDCl_3 . This led us to speculate on the existence of two forms of the compound, one favoured by more strongly solvating solvents e.g. DMSO, and the other by solvents of low dielectric constant e.g. CDCl_3 . Diphenyltelluride proved to be a solvent in which two forms of the compound could

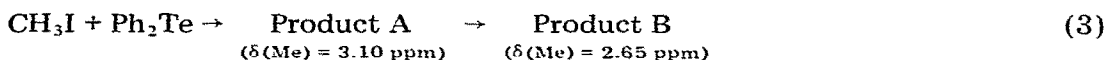
TABLE 2

METHYL RESONANCES (δ vs. TMS) FOR METHYLTELLURONIUM SALTS

Compound	Solvent	Resonance 1 (ppm) ^a	Resonance 2 (ppm) ^b
Ph ₂ (CH ₃)Te(OOCPh)	DMSO- <i>d</i> ₆	2.86	3.85
Ph ₂ (CH ₃)Te(OOCPh)	CDCl ₃	2.96	3.85
Ph ₂ (CH ₃)TeCl	CDCl ₃	2.76	2.96
Ph ₂ (CH ₃)TeBr	CDCl ₃	2.90	2.61
Ph ₂ (CH ₃)Te(NCS)	CDCl ₃	2.90	2.56
Ph ₂ (CH ₃)TeI	CDCl ₃	3.04	2.15
Ph ₂ (CH ₃)TeI	DMSO- <i>d</i> ₆	2.69	2.15

^a Initial resonance - ¹²⁵Te satellites with $J(^{125}\text{Te}-\text{H})$ of 24–25 Hz. ^b Grows with time; due to CH₃X.

co-exist, we therefore followed the reaction of CH₃I with Ph₂Te in excess Ph₂Te (solvent) by ¹H NMR spectroscopy (the temperature of the reaction was 35°C). Immediately after mixing CH₃I with Ph₂Te the only aliphatic resonance was that due to CH₃I at $\delta = 2.15$ ppm, however after 1 min a new resonance of $\delta = 3.10$ ppm is detected, followed by one at 2.65 ppm. The intensity of the MeI resonance decreased to a small constant value after 180 min. The intensities of the three methyl resonances were not appreciably different after 24 h to the values after 180 min. The data are presented graphically in Fig. 1 from which it is noted that the reaction is of the form:



Further, the sigmoidal plot for product B vs. time indicates that it is formed from product A.

(iv) *Molecular weight data.* The rate of reductive elimination of CH₃OOCPh from Ph₂(CH₃)Te(OOCPh) in chloroform was sufficiently slow to make it worthwhile attempting a molecular weight determination by vapour phase osmometry (Knauer osmometer).

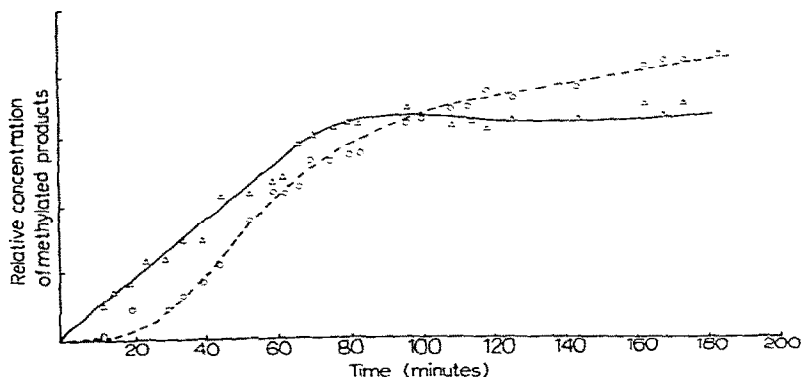


Fig. 1. Plot of growth of methyl resonances at $\delta = 3.05$ ppm (resonance A) and at $\delta = 2.70$ ppm (resonance B) against time for the reaction of methyl iodide with excess diphenyltelluride.

M.W. of $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{OOCPh})$ at 45°C in CHCl_3 : Found: 622, Calcd.: 417.7. This result implies that the salt is not a monomer in chloroform.

(d) *Miscellaneous physical data*

(i) *Infra-red spectra.* IR data was determined with Perkin Elmer 225 and 457 spectrometers. Solids were examined as mulls in Nujol or hexachlorobutadiene and data were obtained for $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{OOCPh})$ in chloroform solution. Data for $\text{Ph}_2(\text{CH}_3)\text{TeI}$, $\text{Ph}_2(\text{CD}_3)\text{TeI}$ and $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{OOCPh})$ are presented in Table 3.

(ii) *Mass spectral data.* Some mass spectra for methyltelluronium salts were obtained with an AEI MS9 mass spectrometer.

(e) *Spin-trapping experiments*

The spin trap used was phenyl-t-butyl nitron (PBN) $\text{PhCH}=\text{N}(\text{O})\text{t-Bu}$, originally introduced by Janzen [10,11], and the experimental method was essentially that developed by Janzen and Blackburn in their study of the photolysis of organolead, -tin, and -mercury compounds [12], with the additional precau-

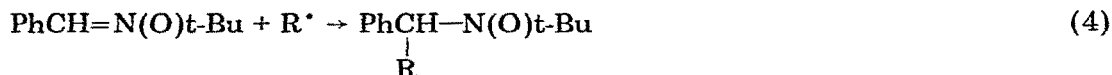
TABLE 3

IR SPECTRA OF CRYSTALLINE $\text{Ph}_2(\text{CH}_3)\text{TeI}$ AND $(\text{CH}_3)_2\text{TeI}_2$ (TOGETHER WITH THE CD_3 COMPOUNDS) BETWEEN 1000 AND 400 cm^{-1} TOGETHER WITH DATA FOR $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{OOCPh})$

$\text{Ph}_2^+\text{Te}(\text{CH}_3)\text{I}^-$	$\text{Ph}_2^+\text{Te}(\text{CD}_3)\text{I}^-$	Δ	$(\text{CH}_3)_2\text{TeI}_2^a$	$(\text{CD}_3)_2\text{TeI}_2$	Δ	Assign-
(1210w)	928w	282	(1223wm)	934w	289	CH_3 symm deformation
(1195w)	916w	279	(1205m)	922m	283	
858m	646m	212	895m	685m	210	
839m	635m	204	848m	640m	208	CH_3 rock
824m	624m	200				
530w	490w	40	527wm	489wm	38	$\nu(\text{Te}-\text{CH}_3)$
523w	483w	40	519w	481w	38	
966s	995s					b or p (phenyl) ^b
838m	839m					g (phenyl)
751m-s	751m					
743s	743s					f (phenyl)
738s	738s					
730s	730s					
686s	686s					ν (phenyl)
666w	666w					r (phenyl)
463ms	463ms					
457m	456m					y (phenyl)
449m	447m					
$\text{Ph}_2\text{Te}(\text{CH}_3)(\text{OOCPh})$						
1600		} 210	(solid state)			$\nu_{\text{as}}(\text{COO})$
1390						$\nu_{\text{s}}(\text{COO})$
1600	CHCl_3 solution		(decays with time)			$\nu_{\text{as}}(\text{COO})$
1720			(grows with time)			MeOOCPh

^a Data and assignments for $(\text{CH}_3)_2\text{TeI}_2$ from ref. 8. ^b Following the notation of Whiffen [9].

tion that the ESR tube was modified as described by Russell, Janzen and Strom [13] to enable solutions to be mixed under anaerobic conditions. The reaction occurring is:



where R^* is a short lived radical. Thus the observation of a signal will indicate the presence of radicals in the reaction mixture, but the identification of the radicals must depend on the measurement of the hyperfine coupling constants a_N (~ 14 Hz) and $a_{\beta H}$ ($\sim 2-3$ Hz). When sharp spectra are obtained these can be measured with some precision, but if the spectra are broader some scatter in the values is noted [12]. We therefore attempted to generate authentic specimens of the suspected free radicals by reaction of Grignard or organolithium reagents with PBN, followed by oxidation with dioxygen [12]; in this way we could "calibrate" our own spectra.

Experimental procedure for organotellurium compounds. Diphenyltelluride was rigorously purified by vacuum distillation, the fraction with b.p. 119–120°C (0.3 mm Hg) being used. The analysis, IR spectrum and mass spectrum indicated purity. All organic halides (commercial) were freshly distilled prior to use. Aliquots of pure benzene (3 cm³) and 0.06 M PBN in benzene (3 cm³) were placed in separate arms of the modified ESR tube and the system was flushed with dinitrogen. In a separate air free flask fitted with a rubber septum, diphenyltelluride (2 molar portions to ensure no precipitation) and the organic halide (1 molar portion) were mixed. Samples of the reaction mixture could be taken after any desired time, added to the benzene solvent arm of the ESR tube which was then inverted to bring the reaction mixture into contact with PBN. ESR signals were observed immediately, however, resolution could be much improved by the brief passage of dioxygen followed by the further passage of dinitrogen for 15 min. In one experiment a benzene solution of $\text{Ph}_2(\text{CH}_3)\text{Te}$ (NCS) was mixed with a PBN solution, this also gave positive evidence for radicals.

Unless deliberately introduced, all solutions were kept dioxygen free, also no

TABLE 4

DATA FROM SPIN-TRAPPING EXPERIMENTS INVOLVING PHENYL-t-BUTYLNITRONE

Reactants	a_N	$a_{\beta H}$	R
$\text{Ph}_2\text{Te} + \text{CH}_3\text{I}$	14.54	2.06	$\dot{\text{C}}\text{H}_3$
$\text{Ph}_2(\text{CH}_3)\text{Te}(\text{NCS})$	14.49	2.04	$\dot{\text{C}}\text{H}_3$
$\text{Ph}_2\text{Te} + \text{Br}(\text{CH}_2)_4\text{Br}$	14.48	2.06	$\dot{\text{C}}\text{H}_2(\text{CH}_2)_3\text{Br}$
$\text{Ph}_2\text{Te} + n\text{-BuBr}$	14.75	1.92	$n\text{-}\dot{\text{B}}\text{u}$
$n\text{-BuMgBr}$	14.71	1.99	$n\text{-}\dot{\text{B}}\text{u}$
$\text{Ph}_2\text{Te} + \text{sec-BuBr}$	14.63	1.96	$\text{sec-}\dot{\text{B}}\text{u}$
$\text{Ph}_2\text{Te} + t\text{-BuBr}$	14.45	1.92	$t\text{-}\dot{\text{B}}\text{u}$
$\text{Ph}_2\text{Te} + \text{BrCH}_2\text{CH=CHCH}_2\text{Br}$	14.45	1.99	$(\text{CH}_2\dot{\text{C}}\text{HCH})\text{CH}_2\text{Br}$

a_N is the hyperfine coupling to ^{14}N , $a_{\beta H}$ that to the β -hydrogen atom, both are in Hz.

undue exposure to light occurred but it cannot be claimed that the experiments were carried out under light free conditions. Each experiment was repeated several times. Information obtained from the spin trapping experiments is gathered into Table 4. Our values do not agree particularly well with those reported by Janzen for given radicals. We found generally that the spectra were fairly broad placing a good deal of uncertainty on $a_{\beta\text{H}}$. We are satisfied that the internal consistency of our data is good and that radicals have been correctly identified.

Further observations

(i) When pure methyl iodide and pure diphenyltelluride are reacted in 1 : 1 molar ratio, white crystals of $\text{Ph}_2(\text{CH}_3)\text{TeI}$ begin to deposit. In the presence of PBN (added as a benzene solution), no solid is seen even after 8 days.

(ii) The reaction of 1,4-dibromobut-2-ene with diphenyltelluride leads to the formation of Ph_2TeBr_2 (quantitative w.r.t. tellurium [14]), however the presence of PBN inhibits the reaction.

(iii) t-Butylbromide and diphenyltelluride left for over 8 weeks produced a solid identified as Ph_2TeO .

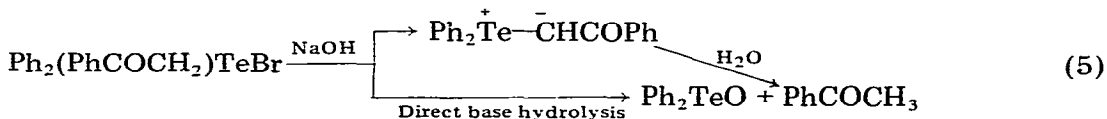
ESR spectra were determined with JEOL JES-PE electron spin resonance spectrometer operating in the X-band and calibrated with a standard Mn^{II} sample diluted with magnesium oxide. Spectra were run at room temperature.

Discussion

(a) Reaction of telluronium salts with base

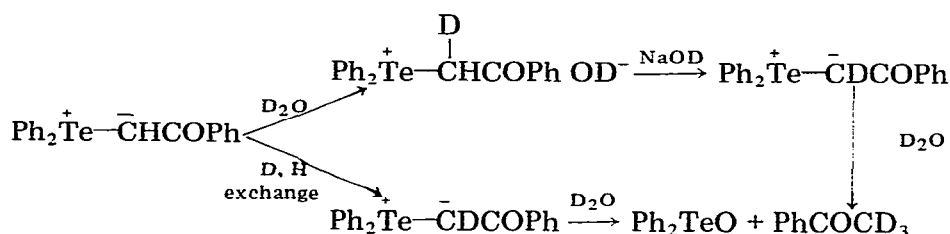
In most instances the rate of reaction 1 was greater than the rate of proton removal from the methylene group, thus no ylid was formed. In one case, however, evidence of ylid formation was obtained.

The salt $\text{Ph}_2(\text{PhCOCH}_2)\text{TeBr}$ (insoluble in chloroform) was treated with aqueous base in the presence of deuteriochloroform in the hope that the ylid would be extracted. Subsequent examination of the chloroform solution indicated that acetophenone (PhCOCH_3) together with Ph_2TeO had been extracted. The acetophenone may arise by one of two routes:



We repeated the experiment using $\text{NaOD}/\text{D}_2\text{O}$ and showed that PhCOCD_3 was formed. We then demonstrated that acetophenone was unaffected by $\text{NaOD}/\text{D}_2\text{O}$ under our conditions, that PhCOCH_2Br (which could arise from dissociation of the salt) afforded PhCOCH_2D and that the hydrolysis of $\text{Ph}(\text{PhCOCH}_2)\text{TeCl}_2$ in $\text{NaOD}/\text{D}_2\text{O}$ also gave PhCOCH_2D . Thus base catalysed exchange of acetophenone, pre-dissociation of the telluronium salt and, by implication, direct base hydrolysis of the $\text{Te}-\text{CH}_2$ - linkage do not provide satisfactory explanations of the formation of trideuterioacetophenone. An ylid intermediate giving rapid exchange at the carbanionic centre can however accommodate the observations, as could an equilibrium involving an ylid and a telluronium

salt:

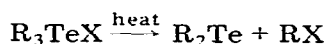


Doering and Hoffmann have offered a similar explanation to account for base catalysed H/D exchange of $[(\text{CH}_3)_3\text{E}]^+$ (E = S, Se, Te) [15].

We were encouraged to continue our efforts to obtain more positive evidence for ylid formation and therefore turned to non-aqueous media selecting triethylamine in chloroform as base. We noted a new resonance at $\delta = 6.3$ ppm which showed the correct 1 : 15 ratio with the aromatic protons. The chemical shift of the ylidic proton in the analogous phosphonium ylid, PhCOCH-PPh_3 is located at $\delta = 4.57$ ppm in DMSO [16]. It can be dangerous to read too much into this difference since the solvents differ.

(b) Reductive elimination of CH_3X from $\text{Ph}_3(\text{CH}_3)\text{TeX}$

The thermal decomposition of triorganotelluronium salts is well known [17] and, more recently, the newly reported triphenyltelluronium pseudohalides have been shown to decompose in a similar fashion on heating [18]:



(X = halide or pseudohalide)

We are not, however, aware of previous reports describing the dissociation equilibria of these compounds in solution.

To simplify the investigation we selected the series $\text{Ph}_2(\text{CH}_3)\text{TeX}$ for study. Using ^1H NMR spectroscopy of chloroform solutions we were able to show that the rate of dissociation (equation 2) was in the order:



In the case of $\text{X} = \text{Cl}$ and PhCOO an equilibrium was established but in other cases the dissociation is complete, thus the stability of the salt to dissociation in chloroform is inversely related to the electronegativity of the ligand atom of the anion.

No marked evidence of dissociation was found in DMF or DMSO although solutions of $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{OOCPh})$ in DMSO which had been left for some days did show evidence of some methylbenzoate. The conductivity of the salts was studied as a function of concentration in both DMSO and DMF (Table 1). In all cases appreciable ion pairing is noted but, in DMSO at least, the values of Λ_M approach values expected for 1 : 1 electrolytes in more dilute solutions. Low conductivities in DMF have also been observed by other workers [19]. Thus, particularly in the strongly solvating DMSO, it would appear that the description "ionic" is justified but even in this solvent considerable association is likely at higher concentrations. Actually, the chemical shift of the methyl

group of $\text{Ph}_2(\text{CH}_3)\text{TeX}$ in DMSO does not vary much with X (Table 2 and ref. 3), hence a viable model for the salt in this medium would be an equilibrium between solvent separated ion pairs and free solvated ions.

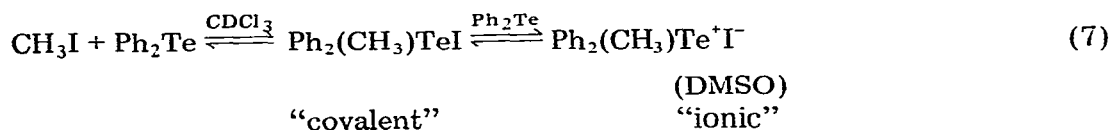
By contrast the methyl resonance of $\text{Ph}_2(\text{CH}_3)\text{TeX}$ is strongly dependent on X in chloroform solution (Table 2), in fact it is reasonable to propose that the groups are electronically coupled i.e. that an element of covalency exists in the Te - - X interaction. Infra-red data were used by Musa [3] to further support the concept of covalency for $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{NCS})$ in chloroform. We have prepared $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{OOCPh})$ and note that in the solid state spectrum the separation of $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ is 210 cm^{-1} which strongly suggests a considerable interaction of the carboxylate with tellurium. Given that ν_{as} occurs at the same frequency (1600 cm^{-1}) in chloroform, it seems that the strength of the interaction is similar in this medium.

Although crystallographic data on telluronium salts are relatively sparse, in most cases studied there is evidence of positive anion—cation interaction. In $[(\text{CH}_3)_3\text{Te}][(\text{CH}_3)\text{TeI}_4]$ for example, both cationic and anionic tellurium atoms are in distorted six coordinate environments [20], and in the case of the triphenyltelluronium pseudohalides the cation anion interaction is sufficient to impose oligomeric structures of some complexity and fascination [e.g. 21,22]. Indeed, only in one case, $[(\text{CH}_3)_3\text{Te}]\text{BPh}_4$, can the structural determination be said to have shown an ionic compound [23]. In Table 3 we examine some IR data for $\text{Ph}_2(\text{CH}_3)\text{TeI}$ and $\text{Ph}_2(\text{CD}_3)\text{TeI}$. To aid assignment we have included literature data for $(\text{CH}_3)_2\text{TeI}_2$ and $(\text{CD}_3)_2\text{TeI}_2$. It will be noted that the observation of two $\nu(\text{Te}-\text{CH}_3)$ modes (530 and 523 cm^{-1}) for $\text{Ph}_2(\text{CH}_3)\text{TeI}$ is incompatible with the most simple ionic model, hence here too there is a strong indication of at least weak anion—cation interaction with at least two such units in the unit cell.

It now seems reasonable that there should be a covalent form of the "salt" in solvents of low dielectric constant. Molecular weights would be useful, but these are complicated by the fact we have dissociation in chloroform. The only salt that could be used for molecular weight determination was the benzoate and it is significant that, despite some dissociation, a value considerably in excess of that for monomeric $\{\text{Ph}_2(\text{CH}_3)\text{Te}(\text{OOCPh})\}$ was obtained. (In a parallel study of stable salts we find many to be accurately dimers in chloroform solution [14]). It therefore appears that dissociation of CH_3X from $\text{Ph}_2(\text{CH}_3)\text{TeX}$ in chloroform may occur from a dimer. This could help to explain another anomaly. If we argue that we have a more "ionic" form of the compound in DMSO, and a more "covalent" form in chloroform, then if we deal with monomers the methyl protons should be more deshielded in DMSO, whereas the reverse is true (Table 2). Since we are unlikely to be dealing with monomers in chloroform and given the implied strong cationic solvation in DMSO further speculation concerning methyl group shielding is of limited value.

The above arguments leading to the suggestion of "ionic" and "covalent" forms of the salt lead to the possibility that these may be capable of coexistence in a solvent of intermediate solvating power. We believe that data obtained for the reaction of methyl iodide in excess diphenyltelluride (solvent) indicate that diphenyltelluride is such a solvent. Thus when the reaction is followed by ^1H NMR spectroscopy the initial methyl resonance at $\delta = 2.15\text{ ppm}$

(CH₃I) diminishes with time to be replaced first by one at $\delta = 3.05$ ppm (resonance A) which grows to a maximum intensity and then diminishes slightly to an equilibrium value; and more slowly by one at $\delta = 2.70$ ppm (resonance B) which rises to an equilibrium value in a sigmoidal fashion (Fig. 1) i.e. there is excellent evidence that the species responsible for B is formed from that responsible for A. The relative intensities of resonances A and B were not significantly different after 24 h to the situation after 180 min. It may be coincidental that resonances A and B (both of which show couplings of ~ 24 Hz to ¹²⁵Te) correspond well in position to the resonances of Ph₂(CH₃)TeI in CDCl₃ (A) and DMSO (B). We believe this observation to be significant and that we are observing an equilibrium between the more covalent and the more ionic form of the compound:



As indicated, by varying the solvating powder of the solvent the equilibrium position in equation 7 may be shifted. We further contend that oxidative addition of CH₃I to Ph₂Te affords, initially, a covalent molecule and that there is a strong parallel with oxidative additions of alkyl halides to Sn{CH(Si(CH₃)₃)₂}₂ and Sn{N(Si(CH₃)₃)₂}₂ [24,25] (in the case of the tellurium system, aryl halides are unreactive; nor is PhX ever eliminated from Ph₂(CH₃)TeX). We considered the possibility of following the reaction by monitoring change of conductivity. If the ionic form is associated with resonance B the rise in conductivity would be sigmoidal with time (as the concentration increases it is likely ion pairing will increase and that the conductivity will fall). If B is due to a covalent form, the conductivity would rise smoothly, then fall. Thus the crucial observation would be the nature of the curve during the initial stages. Unfortunately, conductivities are so low in the viscous Ph₂Te that it was quite impossible for us to make the measurements with adequate precision for our purpose and our case must rest on the NMR study.

(c) Mechanistic considerations

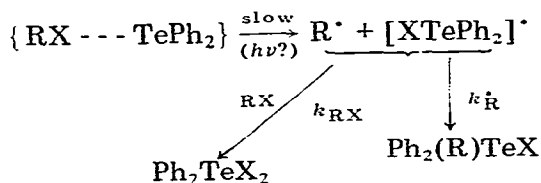
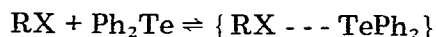
We have suggested [3] that the elimination of CH₃SCN from Ph₂(CH₃)Te-(NCS) may proceed via a radical pathway. Further observations are detailed in the Experimental section of this paper which increase the circumstantial evidence for the proposition that radicals are involved in both the reductive elimination and oxidative addition of alkyl halides and pseudohalides described in this paper and in ref. 3. Thus the reaction of 1,4-dibromobut-2-ene with Ph₂Te affords a 100% yield of Ph₂TeBr₂ (based on Ph₂Te) and yet is completely inhibited by phenyl-*t*-butylnitron (PBN). The same radical trap will inhibit precipitation of Ph₂(CH₃)TeI from the reaction of CH₃I and Ph₂Te in 1 : 1 molar ratio. *n*-Butylbromide gives Ph₂TeO (or sometimes {Ph₂TeBr}₂O when reacted with Ph₂Te over a long period (moisture seems important here). We therefore see bromine capture by tellurium and inhibition by a good radical scavenger.

We decided to search for radicals in a more sophisticated way using electron

spin resonance spectroscopy and the spin trap PBN. The method is adequately outlined in the experimental section. Lappert and coworkers have used successfully spin trapping techniques [24] in their study of addition to tin(II) compounds. The presence of Ph_2Te in our solutions produced considerable broadening of the ESR spectra, again a function of increased viscosity, in this instance slowing molecular tumbling in solution. One consequence of this is that the uncertainty in the measurement of the smaller hyperfine parameter ($a_{\beta\text{H}}$) is large. However, following replicate determinations we are confident that radicals have been correctly identified.

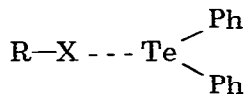
The addition of PBN gave immediate evidence for free radicals. The experiments were carried out under strictly anaerobic conditions, however if dioxygen was then deliberately introduced the concentration of the (same) trapped radical increased. This was experimentally useful in that it gave us a better spectrum to work with, but there is a clear indication that the spin trap not only reacts with the equilibrium concentration of radicals, but also reacts with another species which, on oxidation affords further radicals.

We now have positive evidence for radical pathways in both oxidative addition to Ph_2Te and for reductive elimination from $\text{Ph}_2(\text{CH}_3)\text{Te}(\text{NCS})$. We have not attempted in any one case to prepare the trapped radical species in 100% yield so perhaps we should acknowledge that other pathways may also be involved, although none of our data suggest this to be likely. It is a simple matter to prepare a likely scheme:



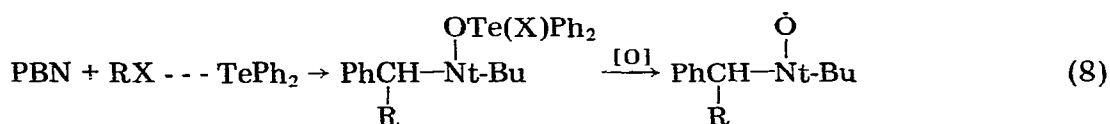
The product depends on the stability of $\text{R}^\bullet$, thus 1,4-dibromobut-2-ene which generates an allylic radical gives entirely Ph_2TeBr_2 . If moisture is present, this may also interfere.

It is necessary, finally, to consider the initiation step. It may be, as Lappert proposes for his tin(II) systems [25], that an interaction between RX and Ph_2Te gives a radical ion pair, $[\text{Ph}_2\text{Te}]^+[\text{RX}]^{\bullet-}$. We are not attracted to this proposal which attributes reducing characteristics to Ph_2Te . We prefer to suggest that a charge transfer complex is initially formed:



which is similar to some proposed in selenium chemistry [8]. Since we have not excluded light from the reaction we would favour photochemical activation of the complex. The postulation of the complex also enables us to suggest an explanation for the observation that the concentration of PBN trapped radicals increases on the passage of dioxygen. If PBN can react with the charge transfer

complex, we have reaction 8:



We therefore conclude that oxidative addition of methyl halides to Ph_2Te proceeds along a radical pathway via the initial formation of a charge transfer complex, and that the initial product of the oxidative addition is a covalent molecule from which, depending on the solvent, ionisation may occur.

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