Isotopic Studies by Vibrational Spectroscopy of the Tellurium–Carbon Bond in Diaryltellurium Dihalides

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Isotopically pure (^{126}Te and ^{130}Te) samples of Ph_2TeCl_2, Ph_2TeBr_2, and $(p\text{-}MeC_6H_4)_2TeBr_2$ have been prepared. Examination of the low-frequency i.r. spectra (with confirmation from Raman spectra) enables definitive assignments of tellurium–carbon stretching vibrations to be made and also establishes this description of these vibrational modes to be physically realistic. The symmetric (Te–Cl) and Te–C) stretching vibrations of Ph_2TeCl_2 are coupled but ν(Te–Br) in Ph_2TeBr_2 is a relatively pure vibration.

We recently presented spectral assignments for the compounds R_2TeX_2 (R = Ph, *p*-MeC_6H_4, *o*-MeC_6H_4, *p*-$MeO\cdot C_6H_4$, and C_6F_5; X = Cl, Br, or I).[1] In that paper we attempted to assign the low-frequency vibrational modes in a semi-empirical manner following the work of Whiffen [2] and previous practice in, particularly, organotin chemistry.[3] We also pointed out that, with a central atom as heavy as tellurium, the Whiffen *t* mode would correspond most closely to ν(TePh) in the phenyl compounds; [4] however, it remained a matter for debate whether this was a meaningful description. Similar problems had existed in co-ordination chemistry for some years, *e.g.* debate as to the reality of ν(MN) in a tris(2,2′-bipyridyl)metal complex; however Nakamoto and his group [5] have now solved many of the problems by application of the conceptually simple but elegant metal-isotope technique.[6] The results in the case of the bipy compounds [5] established that, despite the complexity of the ligand, the description ν(MN) may be realistically applied to some bands in the spectrum and that, furthermore, these bands appear to follow the selection rules of the skeletal point group.

We became interested in placing our assignments, particularly of ν(TeC), for some organotellurium compounds on a firmer experimental footing and therefore decided to use the isotopic technique for the series R_2TeX_2 (R = Ph or *p*-MeC_6H_4; X = Cl or Br). This also provided an opportunity to evaluate the feasibility of the technique for such organometallic compounds, a necessary exercise since economic constraints require that synthetic work involving several stages should be

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[1] W. R. McWhinnie and M. G. Patel, *J.C.S. Dalton*, 1972, 199.

[2] D. H. Whiffen, *J. Chem. Soc.*, 1956, 1350.

[3] J. R. May, W. R. McWhinnie, and R. C. Poller, *Spectrochim. Acta*, 1971, **A27**, 969.

[4] G. Varsanyi, ' Vibrational Spectra of Benzene Derivatives,' Academic Press, New York, 1969, p. 266.

[5] B. Hutchinson, J. Takemoto, and K. Nakamoto, *J. Amer. Chem. Soc.*, 1970, **92**, 3335.

[6] K. Nakamoto, *Angew. Chem. Internat. Edn.*, 1972, **11**, 666.

carried out with pure tellurium isotopes (^{126}Te and ^{130}Te) on a milligramme scale.

EXPERIMENTAL

A number of possible routes to the aryl–tellurium bond were evaluated using 10—20 mg quantities of tellurium of natural isotopic constitution. The methods use either tellurium or a tellurium tetrahalide as starting material. In the latter case $TeCl_4$ was produced by reaction of tellurium with $SOCl_2$. This reaction worked well with small quantities of tellurium. Tellurium tetrabromide was prepared by direct bromination of tellurium.[7] Below we list the methods tried together with brief comment. All reaction mixtures were examined by t.l.c. on alumina plates.[8]

Methods starting with Tellurium.—The reaction of tellurium with tetraphenyltin [9] for 80 h at 220 °C is reported to give diphenyl telluride. We recovered only unreacted starting materials. The reaction of phenyl-lithium with tellurium has been used as a route to diphenyl ditelluride,[10] but on the milligramme scale unacceptably large quantities of biphenyl were produced. Biphenyl was again a major product when diphenyliodonium iodide and tellurium reacted on a small scale, although this reaction has been used to obtain diphenyl telluride.[11]

Vibrational spectra * of some isotopically pure organotellurium compounds below 400 cm^{-1}

Ph_2TeCl_2				Ph_2TeBr_2				(p-$MeC_6H_4)_2TeBr_2$				Assignment
I.r.		Raman		I.r.		Raman		I.r.		Raman		
^{126}Te	^{130}Te	^{126}Te	^{130}Te	^{126}Te	^{130}Te	^{126}Te	^{130}Te	^{126}Te	^{130}Te	^{126}Te	^{130}Te	
286·5	*284·5*	*289*	*287*	160	160	158·5	158·5	168 *or*	168 *or*	165 *or*	165 *or*	
								156	156	156	156	ν_{sym} (TeX)
265	*263·5*	*267·5*	*267*	186(br)	185	184		174(sh)	172(sh)	175	175	ν_{asym}(TeX)
271	*270*			*272*	*270*	*274*	*273*	*299*	*297*			ν_{asym}(TeC) (t)
251(sh)	251(sh)	250	250	258	258	260	260					u(phenyl)
246	*244·5*	*243*	*241*	*241·5*	*240*	*241*	*240·5*	*239·5*	*238*	*240·5*	*239·5*	ν(TeC)$_{sym}$ (t')
229·5	229·5	235	235									u'(phenyl)
226	226											
185	185		184	186br	185	184						x(phenyl)
								257(sh)	257(sh)			
								251(sh)	251(sh)			
135	135							215	215			
								205	205	203	203	
123	123							144	144			

* Bands which shifted on isotopic substitution are shown in italics.

Methods starting with a Tellurium Tetrahalide.—The well known Grignard route [12] worked successfully until the hydrolysis stage when unacceptable quantities of tellurium were deposited (a common problem with this reaction in organotellurium chemistry). The direct reaction of tellurium tetrahalides with aromatic ethers is well known.[13] However, reaction of the tetrahalide with methyl (or ethyl) phenyl ether gave mixtures of products from which it was not possible to extract adequate yields of the diorganotellurium dihalide.

The successful method was that recently reported by Pant [14] involving organolead intermediates [equation (1)].

$$TeX_4 + R_4Pb \longrightarrow R_2TeX_2 + R_2PbX_2 \qquad (1)$$

The best yields (based on 10 mg of isotopically pure tellurium) were for $TeCl_4$ and Ph_4Pb (50%); $TeBr_4$ gave lower yields. The yield of (p-$MeC_6H_4)_2TeBr_2$ was quite good (*ca.* 30%), but the reaction of $TeBr_4$ with (o-$MeC_6H_4)_4Pb$ gave a very poor yield. Tetra(o- and p-tolyl)-lead were prepared following Gilman and Bailie.[15] The compounds prepared for study were $Ph_2{}^{126}TeCl_2$, $Ph_2{}^{130}TeCl_2$, $Ph_2{}^{126}TeBr_2$, $Ph_2{}^{130}TeBr_2$, (p-$MeC_6H_4)_2{}^{126}TeBr_2$, and ($p$-$MeC_6H_4)_2{}^{130}TeBr_2$. The materials were shown to be pure by comparison of i.r. spectra with authentic samples containing tellurium of natural isotopic abundance and by mass spectrometry.

Measurement of Spectra.—The i.r. spectra were determined for pressed Polythene discs by replicate scans on a Perkin-Elmer 225 spectrometer and on a R.I.I.C. FS 720 interferometer (both instruments were calibrated using water vapour). Raman spectra of the crystalline samples were obtained using a Coderg PH1 spectrometer with 632·8 nm (He–Ne laser) excitation. The Raman data were obtained by courtesy of Dr. D. M. Adams at the University of Leicester. The Raman spectrometer was calibrated using non-lasing He–Ne lines. Shifts of bands of 1 cm^{-1} or more could be measured with confidence.

RESULTS AND DISCUSSION

The low-frequency vibrational data (Table) showed satisfactory agreement with figures quoted for the same compounds of natural isotopic abundance by McWhinnie and Patel.[1] Some bands were less broad; this led to the recognition of a definite shoulder at 251 cm^{-1} in the i.r. spectrum of Ph_2TeCl_2 which was confirmed by observation of a weak feature in the Raman spectrum at $\Delta\nu$ 258 cm^{-1}. It was noted that some bands underwent definite shifts of between 1 and 2 cm^{-1} whereas others were completely insensitive to substitution of ^{126}Te by ^{130}Te. The significance of these shifts is now briefly discussed.

Two bands above 200 cm^{-1} shifted in the spectrum of Ph_2TeBr_2 (*ca.* 270 and *ca.* 240 cm^{-1}). These must then

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[7] H. E. Cocksedge, *J. Chem. Soc.*, 1908, 2175.

[8] M. Vobecky, V. D. Nefedov, and E. N. Sinotova, *Zhur. obshchei Khim.*, 1965, **35**, 1684.

[9] M. Schmidt and H. Schumann, *Z. Naturforsch.*, 1964, **B19**, 74.

[10] J. L. Piette and M. Renson, *Bull. Soc. chim. belges*, 1970, **79**, 353.

[11] R. B. Sandin, F. T. McClure, and K. Irwin, *J. Amer. Chem. Soc.*, 1939, **61**, 2944.

[12] H. Rheinboldt and N. Petragnani, *Chem. Ber.*, 1956, **89**, 1270.

[13] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 1925, 2307.

[14] B. C. Pant, *J. Organometallic Chem.*, 1973, **54**, 19.

[15] H. Gilman and J. C. Bailie, *J. Amer. Chem. Soc.*, 1939, **61**, 731.

be assigned as the t and t' modes and may also realistically be described as ν_{asym}(TeC) and ν_{sym}(TeC). It was noted that bands at 270 and 245 cm^{-1} underwent shifts in the spectrum of Ph_2TeCl_2 and are thus ν(TeC). It may be noted that in the earlier empirical study the 258 cm^{-1} band of Ph_2TeBr_2 was assigned as t and that at 243 cm^{-1} as u; it is now clear that this assignment must be reversed. The spectra of (p-$MeC_6H_4)_2TeBr_2$ also showed that two bands shifted on isotopic substitution; thus the reality of the concept of ν(TeC) may be carried over to compounds containing more complex aryl groups.

Two tellurium–chlorine stretching vibrations are expected above 200 cm^{-1} for Ph_2TeCl_2 [1] and, indeed, bands at 286 and 265 cm^{-1} underwent shifts on isotopic substitution (the composite nature of the Raman band at $\Delta\nu$ 267 cm^{-1} has been discussed previously [1]). Thus the previous assignments [1] are confirmed. However, it is notable that apparently the (TeBr) modes do not undergo a shift on isotopic substitution. Unfortunately ν_{asym}(TeBr) overlapped with the phenyl x mode at 184 cm^{-1}, thus rendering any conclusions as to shift highly suspect; but ν_{sym}(TeBr) was readily recognised from the pre-resonance enhancement of intensity in the Raman effect and it is quite clear that this band is unaffected by the substitution. The skeletal symmetry of the TeC_2X_2 group is C_{2v}; hence both ν_{sym}(TeC) and ν_{sym}(TeX) are of A_1 symmetry and should couple. The Br–Te–Br angle in Ph_2TeBr_2 is 178°; [16] thus the symmetric (TeBr) stretch should involve little or no motion of the tellurium atom. Any frequency shift of ν_{sym}(TeX) arising from substitution of ^{126}Te by ^{130}Te must arise *via* coupling with ν_{sym}(TeC). The energy of ν(TeC) and ν(TeCl) in Ph_2TeCl_2 are close, hence strong coupling of ν_{sym}(TeCl) and ν_{sym}(TeC) is expected and exemplified by the observation of shifts of both (TeCl) stretching modes. The energy difference between ν(TeC) and ν(TeBr) in Ph_2TeBr_2 is *ca.* 100 cm^{-1}; hence at best only weak coupling will occur so that ν_{sym}(TeBr) is a purer vibration than ν_{sym}(TeCl).

The isotope method has thus given a firmer basis for the assignment in these complex molecules and has established the physical reality of the description ' tellurium–carbon stretch ' in aryltellurium derivatives. Nakamoto observed that bending modes do not generally produce shifts large enough to measure with confidence and such is our experience here. The assignment of t, u, and x modes in the phenyl compounds is now quite definite, but we are unable to suggest why the mode described as u' (Table) should appear with such intensity in the i.r. spectrum of Ph_2TeCl_2 and yet be absent from that of Ph_2TeBr_2 (it is present for Ph_2TeI_2 [1]). We have also demonstrated that the metal isotope method is feasible and economic for the solution of some vibrational problems in organometallic chemistry provided synthetic routes which can be operated on a milligramme scale are available to the desired compounds.

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[16] G. D. Christofferson and J. D. McCullough, *Acta Cryst.*, 1958, **11**, 249.