Aspects of the chemistry of diorgano tritellurides

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Abstract

The synthetic methods available for diorgano tritellurides, which normally give only poor to moderate yields of product, are evaluated. Most reliable when organic groups such as 2-(2'-pyridyl)phenyl- are involved is the reaction of Te^{2-} with the organotellurenyl halide in DMF. Other methods require a final oxidative step. Reactions of Te_2^{2-} with organotellurenyl halides in DMF give deep red solutions which quantitatively deposit tellurium on exposure to air; successful syntheses of $(RTe)_2Se_2$ (R = 2-(2'-pyridyl or 2'-quinolinyl)phenyl-) were carried out by use of Se_2^{2-} in DMF solution. The air stable bis-[2-(p-tolyl-iminomethyl)phenyl] tritelluride is reported, and its ^{125}Te and Raman spectral data presented. The role of intra-molecular coordination in stabilising these molecules may be a secondary one; the steric effect of a bulky 2-substituent on the tellurated phenyl-ring may be more significant.

Key words: Tellurium; Tritelluride

1. Introduction

A few years ago, two reports of structurally characterised diorgano tritellurides appeared almost simultaneously [1,2]. In one case, Sladky *et al.* [1] used the sterically demanding *tris*-trimethylsilylmethyl-group, $(Me_3Si)_3C$-, to achieve kinetic stabilisation of the tritelluride, which was prepared by a route culminating in an oxidation of a supposed intermediate RTeTe⁻ (R = $(Me_3Si)_3C$-). The initial preparation of the other tritelluride [2] was more serendipitous, since it was obtained during an attempt to prepare the organotellurolate directly by reduction of the organotellurium tribromide, but the structure determination for bis-(2-(2'-pyridyl)phenyl tritelluride showed a Te–N interaction of 2.554 Å which, while much longer than the sum of the Pauling covalent radii [3], *viz.* 2.07 Å, is much

shorter than the van der Waals distance of 3.70 Å. In view of this fairly significant Te ← N interaction, it was suggested [4] that the material could be regarded as a bis-(organo tellurenyl)telluride, and that synthesis could best be carried out by a reaction such as the following:

$$2RTeX + Te^{2-} \longrightarrow (RTe)_2Te + 2X^-$$
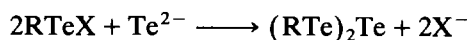
Indeed, the reported synthesis of bis-2-(2'-quinolinyl)phenyl tritelluride [2,4] appeared to provide support for this suggestion.

If the presence of intra-molecular coordination can stabilise polytellurides, there is no obvious reason why this effect should be limited to 2-pyridyl- and 2-quinolinyl- donors. In this paper the opportunity to explore aspects of polytelluride syntheses is taken, and a new tritelluride is reported, which despite giving rise to crystallographic problems, was sufficiently stable in solution for recording of its NMR spectra. The possible synthesis of diorgano tetratellurides is explored and two new bis-(organotellurenyl) diselenides are reported.

TABLE 1. Synthetic approaches to *bis*-2-('-pyridyl)phenyl telluride (R_2Te_3) and to *bis*-2-(2'-quinolinyl)phenyl tritelluride (R'_2Te_3)

R_2Te_3 [a]	m.p. (°C)	Yield (%)
Aerobic/BH_4^-	166–167 (Ref. [4] 165–166)	30
Anaerobic (N_2)/BH_4^-	–	0
via Te^{2-} (DMF/Ar)	166–167	40
R'_2Te_3 [b]		
Ref. [4]	206–207 (Ref. [4] 211–212)	50
via Te^{2-} (DMF/Ar)	208–209	30

[a] Anal. Found: C, 38.4; H, 2.56; N, 3.86. $C_{22}H_{16}N_2Te_3$ calcd: C, 38.2; H, 2.33; N, 4.05%.

[b] Anal. Found: C, 45.2; H, 2.67; N, 3.43. $C_{30}H_{20}N_2Te_3$ calcd: C, 45.5; H, 2.53; N, 3.54%.

2. Experimental details and results

2.1. Synthetic approaches to bis-2-(2'-pyridyl and 2'-quinolinyl) phenyl tritellurides

2.1.1. Bis-2-(2'-pyridyl)phenyl tritelluride

2.1.1.1. Method 1.
The procedure described by Al Salim et al. [4] was used, involving reduction of 2-(2-pyridyl)phenyltellurium(IV) tribromide with sodium borohydride. The product was obtained on exposure of the solution to air. Some decomposition to tellurium occurred, but filtration, washing with ethanol, and recrystallisation from benzene gave a pure product (see Table 1).

2.1.1.2. Method 2.
The same procedure was used except that dioxygen was strictly excluded, an atmosphere of dinitrogen being maintained throughout. The reaction appeared to pursue the same path as that in method 1, but the final red solution that afforded the product in method 1 decomposed instantly to give tellurium (quantitative) and a colourless solution. The procedure was repeated several times with the same observation.

2.1.1.3. Method 3.
The telluride anion, Te^{2-}, may be conveniently generated in dimethylformamide (DMF) solution by reaction of tellurium with two molar equivalents of sodium [5]. Thus, a suspension of tellurium powder (0.32 g, 2.5 mmol) in DMF (40 cm³) was stirred for 1 h under argon. Sodium (0.115 g, 5 mmol) in small pieces was carefully added and the mixture stirred under gentle heat for 1 h. The tellurium dissolved to give a pale yellow solution. A solution of 2-(2'-pyridyl)phenyltellurium(II) bromide was added dropwise and the mixture heated at 60°C for 3 h, during which the solution became pale orange. Cooling to room temperature gave a black solid (Te) in an orange solution. After filtration, the volume of

solution was reduced on a rotary evaporator to give an orange solid, which was recrystallised from benzene to give the pure tritelluride (see Table 1).

2.1.2. Bis-2-(2'-quinolinyl)phenyl tritelluride

2.1.2.1. Method 1.
The procedure was that previously described [4]. Thus to 2-(2'-quinolinyl)phenyltellurium(IV) tribromide [4] (1.14 g, 2 mmol) suspended in absolute ethanol (25 cm³), tellurium powder (0.13 g, 1 mmol) was added, and the mixture was stirred under argon. An excess of sodium borohydride in ethanol (15 cm³) was added dropwise until all the tellurium disappeared to give a red solution, which was refluxed for 30 min., then cooled to room temperature to deposit the orange tritelluride, which was recrystallised from benzene (see Table 1).

2.1.2.2. Method 2.
This was identical with method 3 for *bis*-2-(2'-pyridyl)phenyltritelluride, but the organotellurium reagent used was 2-(2'-quinolinyl)-phenyltellurium(II) bromide.

A summary of the observations from the above preparations is presented in Table 1.

2.2. Attempted syntheses of diorganotellurium tetratellurides and the synthesis of bis-(organotellurenyl)diselenides, $(RTe)_2Se_2$

2.2.1. Method 1
A DMF solution of Na_2Te_2 was generated [5] by stirring a suspension of tellurium (0.255 g, 2 mmol) in DMF (40 cm³) under argon for 1 h at room temperature as sodium (0.046 g, 2 mmol) was added in small pieces. The tellurium slowly dissolved to give a deep-red solution of Na_2Te_2. To this solution was added a solution of 2-(2'-pyridyl)phenyltellurium(II) bromide (1.44 g, 4 mmol) in DMF (20 cm³). The red solution was gently heated at approximately 60°C under argon for 3 h, then the solution was cooled and filtered, whereupon it decomposed spontaneously and quantitatively to Te.

Several variations of the above method failed to bring success.

2.2.2. Method 2
The above method was employed but with 2-(2'-quinolinyl)phenyl-tellurium(II) bromide. Identical observations were made.

2.2.3. Method 3
A suspension of tellurium powder (1.02 g, 8 mmol) in tetrahydrofuran (THF) (40 cm³) was stirred under dinitrogen at room temperature and "superhydride"

(LiBHEt₃) (8 cm³ of a 1 M THF solution, 8 mmol) was added dropwise from a syringe *via* a septum. The mixture was gently heated for 1 h, after which most of the tellurium had dissolved to give a red solution of Li₂Te₂. To this solution was added a solution 2-(2'-pyridyl)phenyl-tellurium(II) bromide (2.88 g, 8 mmol) in THF (30 cm³). The red solution was gently refluxed for 3 h then allowed to cool to room temperature. On filtration in air the solution decomposed quantitatively to tellurium metal.

2.2.4. bis-(2-(2'-Pyridyl)phenyltelluro) diselenide

Selenium powder (0.395 g, 5 mmol) was suspended in warm toluene (30 cm³) and "superhydride" (6 cm³ of a 1 M solution in THF) was added dropwise. The mixture was stirred under dinitrogen for 1 h to give a red solution and an orange suspension. A solution of 2-(2'-pyridyl)phenyltellurium(II) chloride (1.59 g, 5 mmol) in warm toluene (30 cm³) was added dropwise. The mixture was gently refluxed for 3 h, allowed to cool to room temperature, and then filtered. From the filtrate, a bright red solid separated (CAUTION: obnoxious odour). The solid was insoluble in common organic solvents, and decomposed in hot benzene and hot nitromethane. Yield, 80%, m.p. = 230°C (dec.).

Anal. Found: C, 35.9; H, 2.54; N, 3.42. C₂₂H₁₆N₂Se₂Te₂ calcd: C, 36.6; H, 2.24; N, 3.88%.

2.2.5. Bis-(2-(2'-quinolinyl)phenyltelluro) diselenide

Selenium powder (0.395 g, 5 mmol) was suspended in warm dioxane (30 cm³). "Superhydride" (6 cm³ of a 1 M solution in THF) was added dropwise and the mixture was stirred under dinitrogen for 1 h. A solution of 2-(2'-quinolinyl) phenyltellurium(II) chloride (1.84 g, 5 mmol) in warm dioxane (40 cm³) was added dropwise. The mixture was gently heated under dinitrogen for 3 h, then cooled to room temperature. The solution was filtered, and an orange solid separated from the filtrate (CAUTION: obnoxious odour). This material was insoluble in common organic solvents and decomposed in hot nitromethane. Yield 80%, m.p. = 150°C.

Anal. Found: C, 44.2; H, 2.51; N, 3.49. C₃₀H₂₀H₂ Se₂Te₂ calcd: C, 43.9; H, 2.45; N, 3.41%.

2.3. Bis-[2-(p-tolyliminomethyl)phenyl]-tritelluride

The reaction with an excess of borohydride of organotellurium(IV) compounds containing the azomethine group, -CH=N-, generally results in the reduction of both the tellurium(IV) centre to tellurenyl halide or ditelluride and also of the azomethine group to -CH₂-NH- [6]. However the *in situ* generation of NaHTe [7] gave different results. Tellurium (1.0 g) in suspension in refluxing absolute ethanol (15 cm³) was

treated under argon with NaBH₄ (0.75 g, 14 mmol) in ethanol (20 cm³). When the tellurium had dissolved, heating was discontinued and a solution of 2-bromotellurenylbenzal-4'-methylaniline in benzene (40 cm³) was added dropwise. The mixture was gently heated under argon for 0.5 h and then exposed to air during a further 0.5 h, during which an orange suspension formed in an orange solution. Slow filtration yielded a deep-red solution, which was set aside overnight to give a precipitate of small bright red crystals. The solid was collected, washed with hexane, and dried. Yield: 0.97 g, = 36%.

Anal. Found: C, 43.3; H, 3.25; N, 3.58. C₂₈H₂₄N₂Te₃ calcd: C, 43.6; H, 3.15; N, 3.63%. M.p. 130°C. The material is air stable but decomposes in polar solvents with the extrusion of tellurium.

2.4. Physical measurements

The ¹H NMR (300 MHz) and ¹²⁵Te NMR (94.734 MHz) spectra were obtained with a Brüker AC300 spectrometer. Chemical shifts are relative to SiMe₄ (¹H) and Me₂Te (¹²⁵Te). Infrared spectra were obtained with a Perkin Elmer 1710 FTIR spectrometer and Raman data were obtained with a Perkin Elmer FT 1700X Raman instrument using a Nd-YAG laser (1064 nm) and an InGaAs NIR detector cooled to 77 K.

3. Discussion

Since the initial reports of the syntheses of diorganotritellurides [1,2] there has been little additional activity in the area. We recently decided to carry out a survey of possible synthetic methods. The results described in the experimental section and Table 1 reveal that the most reliable route to R₂Te₃ (R = 2-(2'-pyridyl)- and 2-(2'-quinolinyl)phenyl) involves reaction of the tellurenyl halide RTeX (X = Cl, Br) with Te²⁻. This lends credibility to the suggestion that the tritellurides are best regarded as *bis*-organotellurenyl tellurides [4]. However, the yields obtained are only poor to moderate.

Use of borohydride to reduce RTeX₃ is easier to carry out, but the method is unreliable and unpredictable. It is clear that for the method to work the red solutions generated by BH₄⁻ reduction must be exposed to dioxygen. This suggests that an alternative mechanism is operative. It is of interest that when R = 2-(2'-quinolinyl)phenyl, BH₄⁻ reduction of the tribromide gives only the ditelluride, but addition of a half molar proportion of tellurium to the reactants gives the tritelluride.

The fact that diorgano tritellurides can be formed from the reaction shown in eqn. (1):

$$2RTeBr + Te^{2-} \longrightarrow (RTe)_2Te + 2Br^- \qquad (1)$$

suggested that tetratellurides might be obtained if RTeX were treated with Te_2^{2-}. Of the various methods available for the generation of Te_2^{2-} that developed by Sandman *et al.* [5] and the route using "superhydride" ($LiBHEt_3$) were favoured. In all cases deep-red solutions were obtained following the addition of the tellurenyl halide, but exposure to air led to the quantitative deposition of tellurium. By contrast, generation of Se_2^{2-} followed by reaction with RTeBr (R = 2-(2'-pyridyl)- and 2-(2'-quinolinyl)phenyl-) gave air stable materials which analyse as $(RTe)_2Se_2$. There is thus circumstantial evidence that R_2Te_4 may have been formed in solution under strictly anaerobic conditions. The *bis*-(organotelluro) diselenides were very insoluble in all common organic solvents except hot nitromethane in which they decomposed. Thus, no crystals suitable for X-ray could be obtained.

In conclusion, it appears that the solutions generated in polytelluride chemistry are complex, particularly when BH_4^- is used as reductant. Clearly when BH_4^- is used an oxidative process eqn. (2) is required for tritelluride formation, *e.g.*:

$$RTe^- \xrightarrow{Te} RTeTe^- \xrightarrow[RTe^-]{[O]} R_2Te_3 \qquad (2)$$
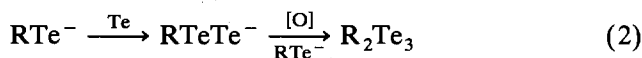
The systems are clearly complex, and under different circumstances either eqn. (1) or eqn. (2) may dominate.

If intra-molecular coordination (Te ← N) is indeed a factor in the stabilisation of the above tritellurides, the isolation of other examples of the species should be possible. The synthesis of *bis*-[2-(p-tolyliminomethyl)-phenyl] tritelluride has now been achieved *via* the reaction of NaHTe, performed under argon, with (*p*-MeC₆H₄·N=CH·C₆H₄)TeBr. In this case, the final stage of the reaction required exposure to dioxygen. The material was crystallised with difficulty but, to date, all crystals examined by X-ray methods have been twinned. Sufficient progress has been made to confirm that the molecule is a tritelluride, but problems with refinement remain [8].

Good quality spectroscopic data have been obtained, in particular Raman and ^{125}Te NMR (Table 2). ^{125}Te NMR were obtained for C_6D_6 solutions, because solutions in $CDCl_3$ are less stable. The concentration was not high, and resolution of satellites was poor but approximate values of $J(^{125}Te-^{125}Te)$ of about 100 Hz were observed, but this value is lower than those observed for unsymmetrical diarylditellurides [9], *e.g.* approximately 170 Hz. Both resonances are deshielded with respect to those for Me_2Te, but that for the terminal tellurium atoms, $\delta = 740.5$ ppm, is significantly more deshielded, as would be expected if these atoms were more electropositive.

TABLE 2. Spectroscopic data for *bis*-2-(p-tolyliminomethyl)phenyl tritelluride

ν (C ≡ N) (cm^{-1})	ν (TeTeTe) (cm^{-1})	^{125}Te NMR [a] (δ ppm *vs.* Me₂Te)
1611 (IR) (m)	202 (R) (m)	432.1 (intensity = 1)
1614 (R) (w)	159 (R) (m)	740.5 (intensity = 2)
1594 (R) (v.s.)		

[a] C_6D_6 Solution. Solutions in $CDCl_3$ decomposed with release of Te at more than 40°C, giving, in the ^1H NMR for example, δ(Me) at 2.342 ppm (major) and 2.364 ppm (minor). IR = infrared, R = Raman.

Excellent quality Raman data were obtained, which enabled assignments of the two expected (Te–Te) stretching vibrations at 202 cm^{-1} and 159 cm^{-1}; these frequencies compare with the range of 167–187 cm^{-1} observed for ν(TeTe) for a selection of diarylditellurides [10], possibly implying that the Te–Te bonds may be of comparable strength in both di- and tri-tellurides.

An interesting structural comparison is provided by the compounds 2-biphenyltellurium(IV) tribromide [11] and 2-(2'-pyridyl)phenyl tellurium(IV) tribromide [4], both of which are monomeric. In the former case, the substituent phenyl-group occupies a position close to the tellurium atom that effectively blocks the approach of bromine from a neighbouring molecule, so preventing inter-molecular association *via* bromine bridges. In the latter case, a further twist about the aryl-aryl C–C bond places the nitrogen atom of the 2-pyridyl group (which must have similar steric demands to a phenyl-group) 2.224 Å from the tellurium atom. This distance is sufficiently short to imply a coordinate interaction. The opportunity was taken to experiment with a computer package designed to calculate energy minima for molecular conformations. When the structural parameters for *bis*-2-(2'-pyridyl)phenyl tritelluride were introduced, and complete freedom of rotation about the 2-pyridylphenyl- C–C bond permitted, the program produced a minimum in the potential energy for a structure which gave co-planar aryl-rings and a Te–N distance of 2.58 Å (average), close enough to the observed distance of 2.554 Å to suggest that any Te ← N interaction may be only secondary in stabilising the molecule.

Acknowledgments

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