Mercurated and Tellurated Schiff Bases and Phenylhydrazones

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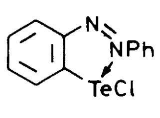
Attempts directly to tellurate Schiff bases or phenylhydrazones result in ionic products arising from hydrolysis of tellurium tetrahalides. However use of mercurated Schiff bases and mercurated phenylhydrazones does afford tellurated derivatives on *trans*-metallation with tellurium tetrabromide or organotellurium trichlorides. [4-Methoxy-2-(phenyliminomethyl)phenyl-*C*^{1},*N*]tellurium(IV) tribromide may be reduced in poor yield to the monobromide. Spectroscopic data (i.r., ^{1}H n.m.r.) are presented and discussed. In particular, ^{13}C n.m.r. spectra were valuable to establish the position of mercuration of the phenylhydrazones.

We have recently synthesised and determined the crystal structure of the *ortho*-tellurated azobenzene (**I**),[1] and shown that it forms a charge-transfer complex with tcnq (tetracyanoquinodimethane)[2] and which possesses unexpected ^{125}Te Mössbauer parameters.[3] Therefore we decided to prepare further examples of aryltellurium halides carrying potentially chelating *ortho* substituents and report in this paper the synthesis of some *ortho*-tellurated Schiff bases (**II**) and phenylhydrazones (**III**) [Y = Me or OMe, X_3 = Br_3 or $Cl_2(C_6H_4OEt$-*p*), R = aryl].

It is interesting that although tellurium tetrahalides will function as electrophiles to, for example, aromatic ethers,[4] compounds such as (**I**)—(**III**) are generally prepared by indirect methods. For example, (**III**) was obtained *via* mercurated azobenzene. Difficulties were experienced in the direct telluration of Schiff bases, hence mercurated compounds were prepared, some of which appear to be new.



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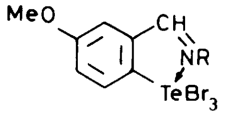

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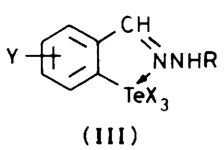

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Experimental and Results

Synthesis.—(*a*) *Schiff bases and phenylhydrazones. m*-Methoxybenzylideneaniline was prepared following a standard procedure[5] as was 2,4-dinitrobenzylideneaniline. A standard method was also used for the preparation of three phenylhydrazones:[6] benzaldehyde *p*-nitrophenylhydrazone, *p*-methylbenzaldehyde *p*-nitrophenylhydrazone, and *p*-methoxybenzaldehyde *p*-nitrophenylhydrazone. All compounds gave satisfactory analyses and spectra.[7]

(*b*) *Mercurated derivatives.* [4-*Methoxy*-2-(*phenyliminomethyl*)*phenyl*-C^1,N]*mercury*(II) *chloride*, (**6**). *m*-Methoxybenzylideneaniline (10.55 g, 50 mmol) and mercury(II) acetate (15.99 g, 50 mmol) were placed in a round-bottomed flask with dry methanol (250 cm^3). The reaction mixture was stirred under reflux for 24 h then cooled. Lithium chloride (5.0 g, 120 mmol) in warm methanol was added and the resulting precipitate was filtered off, washed with diethyl ether, and dried *in vacuo*. Recrystallisation from chloroform gave a colourless *solid* of m.p. 140—142 °C in 40% yield. A chloroform-insoluble material was obtained of m.p. 172 °C (decomp.). This was shown by analysis to be a dimercurated species.

[3,5-*Dinitro*-2-(*phenyliminomethyl*)*phenyl*-C^1,N]*mercury*(II) *chloride*, (**7**). This was prepared by a similar method. Mercuration of the phenylhydrazones was carried out by an adaptation of a literature method.[8]

Analytical and relevant i.r. data are included in Table 1 for the mercurated derivatives.

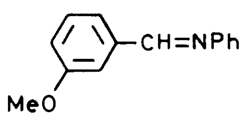
(*c*) *Compounds containing tellurium.* Tellurium(IV) chloride was obtained from B.D.H. Tellurium(IV) bromide[9] and iodide[10] were made by literature methods.

Attempted direct telluration of a Schiff base. To a solution of *m*-methoxybenzylideneaniline (2.11 g, 10 mmol) in dry benzene (50 cm^3) was added tellurium tetrachloride (2.69 g, 10 mmol). The reaction mixture was stirred and refluxed for 5 h. The yellow *precipitate* was filtered off, washed with dry ether, and dried *in vacuo* to m.p. 180 °C. Subsequent examination of this material showed it to contain the protonated base, *m*-$MeOC_6H_4CH{=}\overset{+}{N}HPh$. Use of $TeBr_4$ gave salts of the type [*m*-$MeOC_6H_4CH{=}NHPh]_2[TeBr_6]$. Synthesis of the Schiff base in the presence of tellurium tetrahalides also failed to give tellurated products.

Attempted synthesis of [4-*methoxy*-2-(*phenyliminomethyl*)-*phenyl*-C^1,N]*tellurium*(IV) *trichloride*. Compound (**6**) (0.85 g, 2 mmol) and tellurium tetrachloride (0.34 g, 2 mmol) were refluxed in sodium-dried 1,4-dioxane (20 cm^3) for 4 h under dry dinitrogen. After cooling, the *precipitate* was removed by filtration (m.p. 140 °C). The filtrate was concentrated on a rotary film evaporator but addition of ether produced no further product.

[4-*Methoxy*-2-(*phenyliminomethyl*)*phenyl*-C^1,N]*tellurium*-(IV) *tribromide*, (**15**). A solution of (**6**) (2.14 g, 5 mmol) and tellurium tetrabromide (2.23 g, 5 mmol) in dry chloroform (90 cm^3) was refluxed for 5 h under dry nitrogen. After cooling the reaction mixture to room temperature the precipitated mercury(II) halides were filtered off, and the filtrate concentrated to 20 cm^3 Addition of ether gave the desired *product*, m.p. 180 °C. Use of tellurium tetraiodide under the same conditions gave an intractable sticky black residue which defied attempts at purification; nor did change of reaction solvent from chloroform to 1,4-dioxane (diox) help.

(4-*Ethoxyphenyl*)[4-*methoxy*-2-(*phenyliminomethyl*)*phenyl*-C^1,N]*tellurium*(IV) *dichloride*, (**19**). Compound (**6**) (1.33 g) and (4-ethoxyphenyl)tellurium(IV) trichloride (1.06 g) were mixed in 1,4-dioxane (20 cm^3). The mixture was stirred under reflux for 3 h. Cooling the mixture gave crystals of $HgCl_2{\cdot}2diox$ which were removed. Concentration of the filtrate, followed by addition of light petroleum (b.p. 40—60 °C) gave the crude product.



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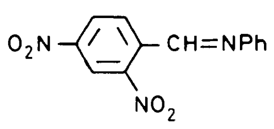

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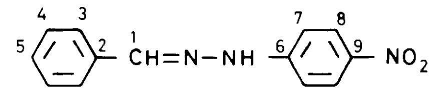

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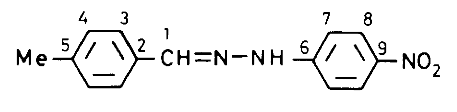

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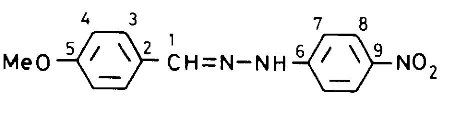

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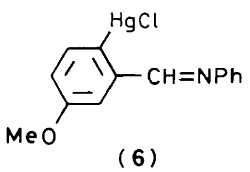

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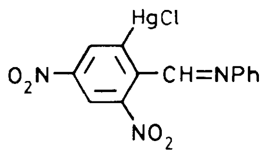

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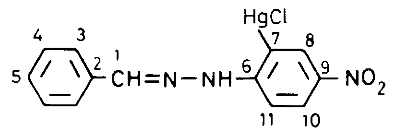

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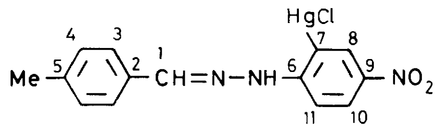

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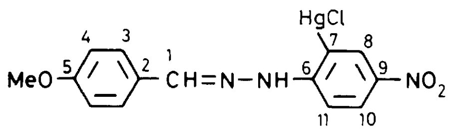

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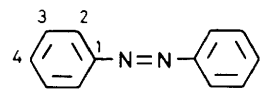

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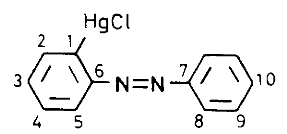

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Table 1. Analytical[a] and i.r. data for organic substrates and their mercurated derivatives

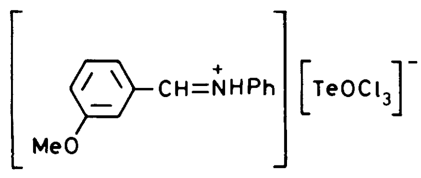
				Analysis (%)			I.r. data (ν/cm^{-1})		
Compound	M.p. (θ/°C)	Colour	Yield (%)	C	H	N	ν(C=N)	ν(CH)	Other
(**1**)	liq.	Colourless	—	79.9 (79.5)	6.20 (6.20)	6.70 (6.60)	1 634s	698vs	—
(**2**)	126	Orange	—	58.1 (57.5)	3.20 (3.30)	15.7 (15.4)	1 600 1 584 }s	775, 765 740, 728, 698	—
(**3**)	192	Brown-red	—	64.8 (64.7)	4.60 (4.50)	16.9 (17.4)	1 608 1 580 }s	748, 740, 712, 680	—
(**4**)	209	Red	—	66.1 (65.8)	5.00 (5.10)	16.2 (16.4)	1 614 1 598 }s	820, 720, 700	—
(**5**)	161	Purple	—	61.6 (61.9)	4.80 (4.80)	15.3 (15.4)	1 620 1 608 }s	840, 830, 721, 700	—
(**6**)	140—142	White	40	37.5 (37.6)	3.00 (2.70)	3.80 (3.10)	1 628s, 1 600(sh)	718, 688	326 ν(HgCl)
(**7**)	172—174[b]	Yellow	90	29.1 (30.8)	1.60 (1.60)	7.60 (8.20)	1 600s	775, 765, 740, 732, 698	—
(**8**)	228—230	Yellow	82	32.1 (32.7)	2.15 (2.10)	8.30 (8.80)	1 600s, 1 580(sh), 1 560s	810, 750, 740, 680	332 ν(HgCl)
(**9**)	238—240	Red	71	33.9 (34.2)	2.60 (2.45)	8.90 (8.50)	1 605s, 1 585s	830, 820, 722, 705	330 ν(HgCl)
(**10**)	224—225	Red	75	33.2 (33.2)	2.40 (2.40)	8.60 (8.20)	1 612s, 1 584s	820, 714	—

[a] Calculated values are in parentheses. [b] With decomposition.

Treatment of the solid with charcoal in boiling chloroform (50 cm^3) gave a pale yellow *product* of m.p. 176 °C.

Successful reactions of $TeBr_4$ and (4-ethoxyphenyl)tellurium(IV) trichloride with three mercurated *p*-nitrophenylhydrazones using the above conditions afforded the corresponding organyltellurium(IV) halides.

*[4-Methoxy-2-(phenyliminomethyl)phenyl-*C^1,N*]tellurium*(II) *bromide*, (**16**). [4-Methoxy-2-(phenyliminomethyl)phenyl-*C*^{1},*N*]tellurium(IV) tribromide (0.43 g) was dissolved in warm methanol (30 cm^3). Hydrazine hydrate in methanol was added dropwise causing the pale yellow solution to become dark red. Some black precipitate was formed (Te) which was removed by



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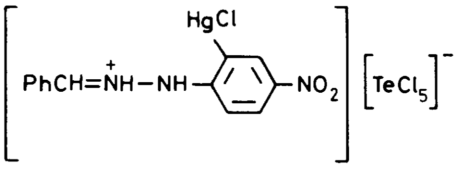

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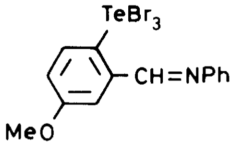

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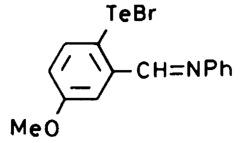

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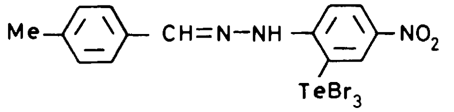

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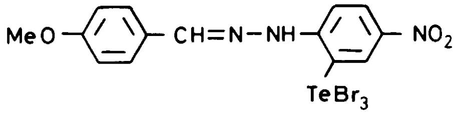

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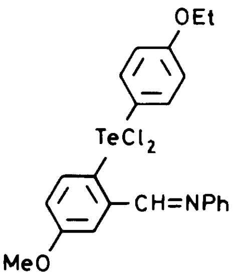

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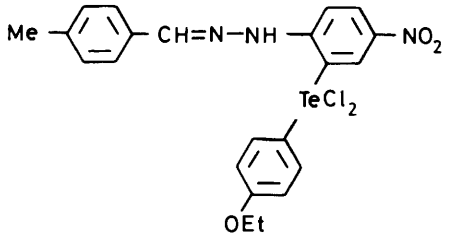

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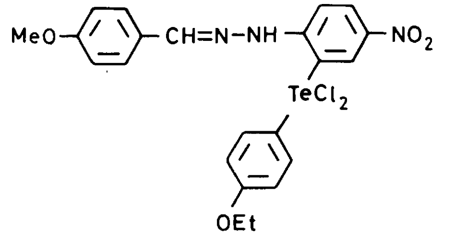

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Table 2. Analytical[a] and i.r. data for new tellurium compounds

				Analysis (%)				I.r. data (ν/cm^{-1})		
Compound	M.p. (θ/°C)	Colour	Yield (%)	C	H	N	Te[b]	ν(C=N)	ν(CH)	Other
(13)[c]	180[d]	Yellow	100	35.0 (36.3)	3.10 (3.00)	3.00 (3.00)	25.3 (27.6)	1 645s, 1 618vs		3 590, 3 530 ν(NH) 610 ν(TeO)
(14)	165[d]	Greenish yellow	100	20.9 (20.4)	1.30 (1.55)	6.10 (5.50)	— —	1 598vs	820, 760, 750, 720, 698	3 500, 3 230 ν(NH) 332s ν(HgCl)
(15)	180	Red	42	28.0 (29.0)	2.20 (2.10)	2.60 (2.40)	22.6 (22.9)	1 624s	721s	
(16)	110[d]	Dark red	30	39.1 (40.2)	2.90 (2.90)	3.80 (3.30)	31.8 (30.5)	1 600s	728s	
(17)	170[d]	Brownish red	40	26.3 (27.0)	1.80 (1.95)	5.40 (6.70)	20.2 (20.5)	1 588m	830, 820, 720, 705	
(18)	120[d]	Brownish red	36	25.6 (26.3)	1.70 (1.90)	5.30 (6.50)	19.7 (20.0)	1 616s	835, 705	
(19)	176—177	Pale yellow	70	50.6 (51.1)	4.00 (4.00)	2.20 (2.70)	23.9 (24.6)			274, 258(sh) ν(TeCl)
(20)	150—151	Yellow	67	45.8 (46.0)	3.60 (3.60)	7.40 (7.30)	21.8 (22.2)			271, 260 ν(TeCl)
(21)	160—162	Dark yellow	63	43.1 (44.7)	3.40 (3.50)	7.50 (7.10)	21.1 (21.6)	1 590s	810, 710	276, 263 ν(TeCl)

[a] Calculated values are in parentheses. [b] Tellurium was analysed following F. H. Kruse, R. W. Sanfter, and J. F. Suttle, *Anal. Chem.*, 1953, **25**, 500. [c] Cl, 22.5 (23.0%). [d] With decomposition.

filtration. The filtrate was reduced by passing a slow stream of dry dinitrogen to evaporate the solvent. The resulting dark red solid was recrystallised from chloroform to give a *product* of m.p. 110 °C (decomp.).

Table 2 gives analytical and i.r. data for the tellurium-containing compounds.

Discussion

Attempts directly to[11] tellurate Schiff bases, *e.g.* *m*-methoxybenzylideneaniline, with tellurium tetrahalides failed despite the presence of the methoxy-group to direct electrophilic attack to the '*ortho*' position.[12] Clearly, despite taking precautions to dry solvents, hydrolysis of the tetrahalides had occurred to give

Table 3. Typical ^{1}H n.m.r. data[a] for mercurated and tellurated compounds

Compound	-CH=N-	$-OCH_3$	$-OCH_2CH_3$	$-CH_3$	Aryl H
(1)	8.2 (s)	3.6 (s)			7.2 (m)
(6)	8.65 (s)	3.9 (s)			7.4 (m)
(15)	9.28 (s)	3.9 (s)			7.5 (m)
(19)	8.8 (s)	3.95 (s)	1.45 (t)[b]		7.0—7.7 (m)
(5)	8.3 (s)	3.8 (s)			6.9—8.0 (m)
(10)	8.1 (s)	3.8 (s)			6.9—8.0 (m)
(4)	8.14 (s)			2.35 (s)	7.0—8.4 (m)
(9)	8.08 (s)			2.30 (s)	6.85—8.35 (s)
(20)	8.15 (s)		3.85 (q, CH_2) 1.30 (t, CH_3)	2.3 (s)	7.0—8.15 (m)

[a] Chemical shifts (δ) relative to $SiMe_4$; in $CDCl_3$. [b] $-OCH_2CH_3$ resonance; $-OCH_2CH_3$ masked.

Table 4. Carbon-13 n.m.r. spectroscopic data[a]

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	Other
(11)	152.4	122.7	128.9	130.7								
(12)[b,c]	143.2	137.7	130.1	128.9	122.5	n.o.	150.9	122.5	129.5	131.7		
(3)	141.6	134.6	125.9	128.6	129.0	150.4	111.1	126.3	138.3			
(8)	142.6	133.9	127.0	128.5	129.3	152.8 (J = 74.2)	132.7 (J = 1 874)	125.1	138.4	134.8	112.4 (J = 148.4)	
(4)	141.9	131.7	126.0	129.6	138.9	150.6	111.0	126.3	138.5			20.9 (Me)
(9)[c]	142.8	131.4	127.0	129.2	138.4	153.3	132.6	134.8	138.4	125.1	112.3	21.0 (Me)
(5)	141.8	127.2	127.9	114.2	160.2	150.6	110.9	126.1	137.9			55.2 (OMe)
(10)	143.0	126.4	128.7	114.0	160.5	153.1 (J = 42.8)	132.3 (J = 2 742)	125.3 (J = 21.5)	138.2	134.9	112.3 (J = 146.5)	55.3 (OMe)

[a] See structures for atom numbering. Chemical shifts are relative to $SiMe_4$. Coupling constants (J) are in Hz. [b] Prepared as in ref. 11. [c] Insufficiently soluble to detect J(Hg–C).

products containing quaternary cations derived from the Schiff bases. Use of the less readily hydrolysed $TeBr_4$ did not help.

The ionic products are of little interest in the context of this paper. We record some data in Table 2 [*e.g.* compound **(13)**] where it is seen that a chloro-oxotellurate(IV) salt is obtained in the case of $TeCl_4$ [ν(Te=O) 610 cm^{-1}]. $TeBr_4$ gave $TeBr_6^{2-}$ salts. The addition of a Lewis acid such as $AlCl_3$, which has been helpful in other contexts,[13] was unable to promote telluration of the base.

Two alternatives were considered: first, the rigorous exclusion of moisture, and secondly a *trans*-metallation reaction involving organomercury derivatives of the Schiff bases and phenylhydrazones. Given that the synthesis of tellurated azobenzenes was successfully achieved *via* the organomercury compounds,[1] the *trans*-metallation route was chosen.

Mercuration of the two Schiff bases proceeded in good yield [compounds **(6)** and **(7)**]. Good i.r. and ^{1}H n.m.r. evidence (Table 3) was obtained to support the *ortho*-mercuration. Mercuration of the phenylhydrazones also proceeded easily [compounds **(8)**, **(9)**, and **(10)**] but in this case the i.r. and ^{1}H n.m.r. spectra could not definitely establish the point of metallation. Carbon-13 n.m.r. spectra were useful, however, and data are given Table 4.

The assignment of carbon atoms bearing mercury was confirmed by the observation of large one-bond coupling constants (seen as satellites on the ^{13}C spectra) and by the relatively low signal intensity due to long relaxation times. Chemical shifts were observed in the range 132—142 p.p.m. In addition, in favourable cases, *ortho*-, *meta*-, and *para*-carbon–mercury-199 coupling was observed with the order $J(HgC_{meta}) > J(HgC_{ortho}) > J(HgC_{para})$ which concurs with data for phenyl derivatives of other heavy atoms.[14]

The assignment of other carbon resonances in Table 4 was assisted by simple additivity relationship values for unsubstituted benzene (128.5 p.p.m.) and monosubstituted benzenes, these being taken from the literature.[15] Inspection of data in Table 4, which includes those for unmercurated phenylhydrazones, leaves little doubt that mercuration has occurred in the position indicated.

The n.m.r. data do not indicate the degree of interaction of the azomethyne nitrogen atom with mercury, but i.r. data suggest the co-ordination to be weak (Table 1).

Attempts to react the mercurated Schiff bases and phenylhydrazones with tellurium tetrachloride again afforded ionic products of which compound **(14)** is representative. However, tellurium tetrabromide did give tellurated derivatives [compounds **(15)** and **(16)**], but use of tellurium tetraiodide gave intractable mixtures. The mercurated compounds also reacted smoothly with organotellurium trichlorides to give the new dichlorides **(19)**, **(20)**, and **(21)**.

I.r. spectra of compounds **(15)** and **(16)** are quite similar to those of the mercury derivatives thus supporting the not unreasonable assumption that telluration has occurred at the point of mercuration. Evidence for the formation of tellurium–nitrogen bonds rests at this time mainly on i.r. data where the 10—30 cm^{-1} shift of ν(C=N) to lower wavenumber is of the same order as the shift in ν(N=N) seen for tellurated azobenzenes where crystallographic support is available for weak Te←N co-ordination in structure **(I)**.[1]

The diorganotellurium dichlorides [compounds **(19)**, **(20)**, and **(21)**] all show ν(TeCl) below 300 cm^{-1} consistent with a basic pseudo-trigonal bipyramidal structure[16] although it is quite conceivable that weak secondary bonds will increase the co-ordination number of the tellurium in the solid state.

The objective of this work was to produce new organotellurium(II) halides, hence it was disappointing that ultimately only reduction of compound **(15)** gave a stable tellurium(II) derivative and even in this instance the yield was poor.

In conclusion, some new tellurated species have been synthesised, but not without difficulty. The tribromides and the monobromide [**(15)**, **(16)**, and **(17)**] provide further examples of organotellurium compounds containing Te–N bonds, a class which remains sparcely populated.

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