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DIARYL TELLUROXIDES AS NEW MILD OXIDISING REAGENTS†

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Abstract— Dianisyltelluroxide (**1**) has been shown to be an especially mild and selective oxidising reagent for a number of organic substrates. Phosphines can be oxidised to their corresponding oxides while thiols are converted to disulphides. Thiocarbonyl compounds can be transformed to their oxo analogues either directly by **1** or by a catalytic cycle involving the use of 1,2-dibromotetrachloroethane as a room temperature brominating agent for various Te^{II} species.

On oxidation acyl hydrazines produce hydrazides in high yield whereas aryl hydrazines afford arenes and symmetrical and unsymmetrical tellurides.

Many other readily oxidised functional groups are inert towards **1**.

Although organosulphur reagents,[1] and in more recent years organoselenium reagents,[2] have been used with success in organic synthesis very few tellurium containing compounds have found useful application.[3]

Here we report in full the use of diaryltellurium (IV) species as mild and selective oxidising reagents.[4] We have focused our efforts mainly on the use of bis(*p*-methoxyphenyl)telluroxide (**1**) for several reasons. Firstly the reagent is easily prepared by basic hydrolysis of the dichloride (**2**) which in turn was readily obtained in 83% yield by treatment of anisole with $TeCl_4$.

The telluroxide (**1**) is soluble in most organic solvents and is stable in the dark at room temperature. Also, in contrast to the unstable and unpleasant dialkyltelluroxides,[5] compound **1** and the corresponding telluride (**3**) are odourless. Lastly Te–O bonds are weaker than, either S–O or Se–O bonds.[6] The observation that the mass spectrum of **1** does not show a molecular ion but has the base peak corresponding to the telluride (**3**), exemplifies this weakness. Thus telluroxides might efficiently transfer oxygen to organic substrates.

It has recently been demonstrated that dimethylselenoxide is a better oxidant than dimethylsulphoxide for certain phosphorus containing compounds.[7] It follows therefore that the telluroxide (**1**) could be even better and that the odourless telluride (**2**), formed as a by-product, could be recovered and reoxidised to **1**.

Accordingly treatment of either tri n-butylphosphine or triphenylphosphine with **1** (1 equiv) at room temperature gave good yields of the corresponding phosphine oxides. The reaction however did not show any substantial improvement over the literature procedures.

Next we investigated the use of **1** to effect the conversion of thiocarbonyl groups to their oxo analogues. Reagents that will effect this transformation are known.[8]

A number of readily available thiocarbonyl and selenocarbonyl compounds (**4** → **14**) were treated with the telluroxide (**1**) and, with a few exceptions, were found to afford their corresponding oxo derivatives (Table 1). The product yields were generally high and elemental S (or Se) was also isolated in each case. Separation of the oxidation product from dianisyltelluride (**3**) was nearly always possible using column chromatography or plc, the exception being the trithiocarbonate (**8**).

Similar reaction of thiocamphor (**15**) with **1** gave a number of products two of which were camphor and the dithione (**16**). The oxo derivatives are undoubtedly formed by similar mechanisms to those proposed in related systems. Compound **16** is most likely derived by oxidation of the thioenol by **1** to the *bis*-vinyldisulphide which slowly undergoes a hetero-Cope reaction[9] (Scheme 1).

Reaction of phenylisothiocyanate with **1** gives diphenylurea on aqueous work up. No attempt was made to isolate the intermediate phenylisocyanate. Although the dianisyltelluroxide (**1**) is only sparingly soluble in water it can be used to convert thiourea into urea using an aqueous system.

This last observation may find application in the modification of certain nucleic acids following the discovery of 4-thiouridine in t-RNA of *E. coli*.[10] Many methods have been used to chemically transform this base.[11]

Another obvious area where new mild oxidants are required is for the conversion of thiols to disulphides.

It has been reported that diorganotellurium dialkoxides[12] and diaryl dichlorides[13] both effectively convert aromatic thiols to disulphides. The dianisyltelluroxide (**1**) should be equally effective. In this case the by-products of the reaction would be water and the inoffensive telluride (**3**) (Scheme 2).

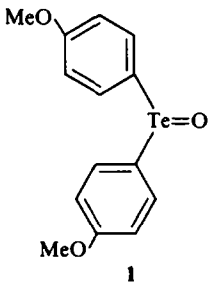
The thiols (**17** → **20**) rapidly react with **1** to give the corresponding disulphides in very high yields. The fact

†Dedicated with respect to the memory of Robert Burns Woodward.

Table 1. Oxidation of thiocarbonyl derivatives by dianisyltelluroxide (1)[a]

Starting material	Reaction time (h)	Yield of oxo-derivative (%)
4a	24	Quant
4b	0.3	93
5a	1.5	66
5b	0.25	Quant
5c	27	70
6a	63	Quant
6b	16	68
7	0.5	96
8	20	a
9	4	91
10	1	98
11	0.75	87
12	42	23
13	0.3	Quant
14	20	87

a) Inseparable from the telluride (3)



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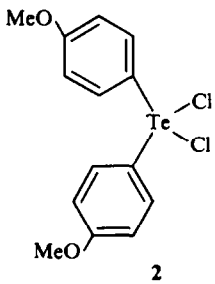

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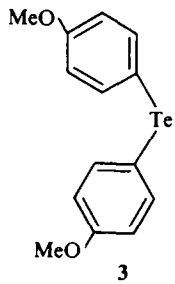

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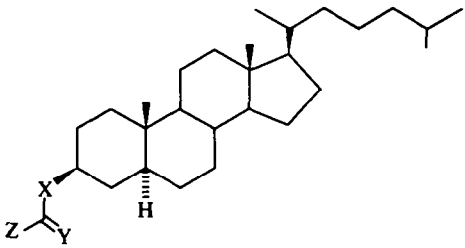
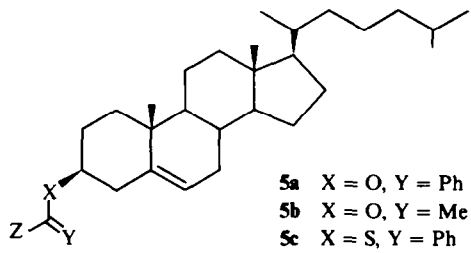


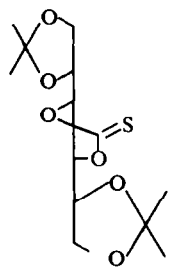
4a X = O, Y = S, Z = SMe
4b X = O, Y = Se, Z = Ph



5a X = O, Y = Ph
5b X = O, Y = Me
5c X = S, Y = Ph

$(RNH)_2C=S$

6a R = H
6b R = Ph



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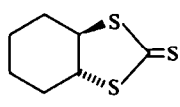

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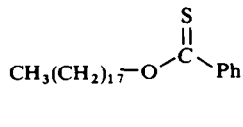

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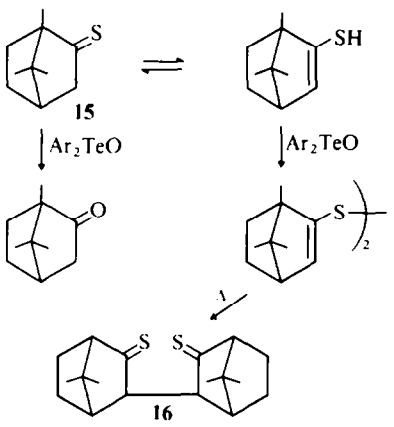
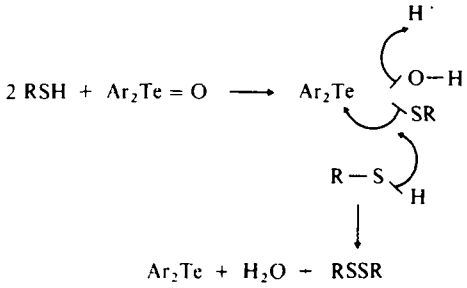


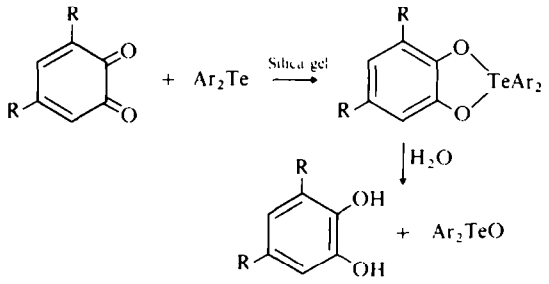
Scheme 1



Scheme 2

that **17** and **20** react to afford disulphides although other easily oxidised functional groups are present demonstrates the mildness of the new oxidant. Other useful procedures have also recently been reported.[14]

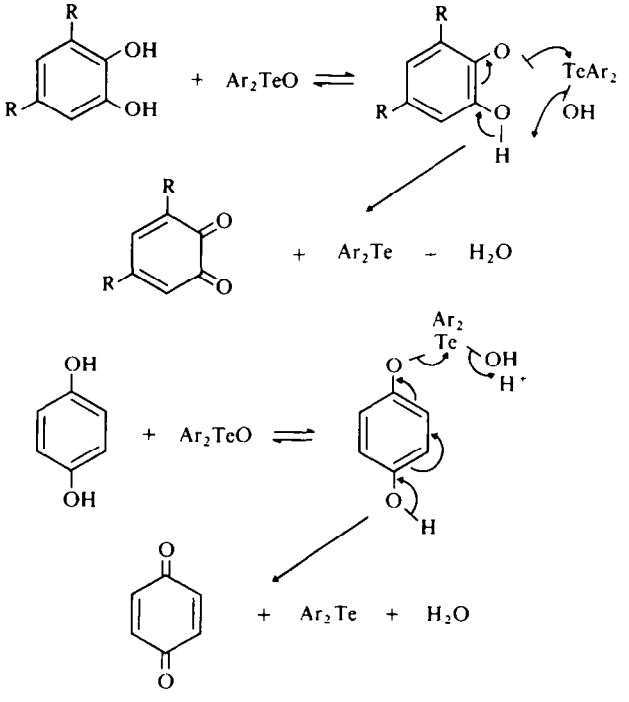
The oxidation of phenols is often a facile process. However many simple monohydroxylic phenols are not oxidised by **1**. Reaction of the hydroquinones (**21** and **22**) and the catechol (**23**) with the telluroxide (**1**) affords the corresponding quinones (**24**–**26**). The mechanism for these oxidations is not clear although a recent report[15] which describes the use of diphenylselenoxide as an oxidant for catechols suggests a selenurane species (**27**) as a possible intermediate. Alternative mechanisms can be proposed (Scheme 3).



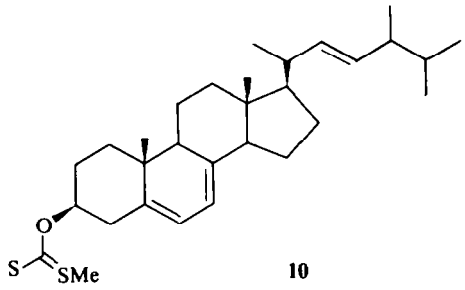
Scheme 4

Theoretically only one equivalent of telluroxide should be necessary for complete oxidation of both catechols and hydroquinones as is in fact found for the oxidation of **21** and **22**. However when the mixture from the oxidation of **23** with 1 equiv of **1** was subjected to plc little or no telluride (**3**) was obtained while the ortho quinone (**26**) was isolated together with unreacted catechol (**23**).

In contrast the ^{1}H NMR spectrum of the crude mixture showed only the presence of the telluride (**3**) and quinone. Only when an excess of telluroxide (**1**) was used could one obtain **26** in acceptable yields. Furthermore if equimolar amounts of pure quinone (**26**) and telluride (**3**) were dissolved in $CDCl_3$ the ^{1}H NMR spectrum showed only these to be present; however if this mixture was analysed by tlc quinone, catechol and trace amounts of the telluride could be detected. These observations suggest that under



Scheme 3



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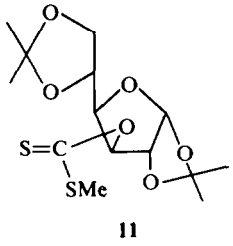

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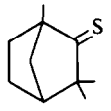

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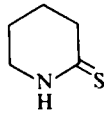

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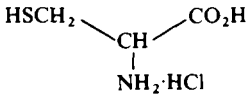

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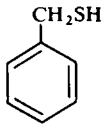

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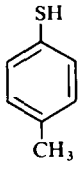

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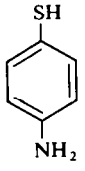

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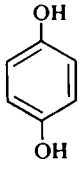

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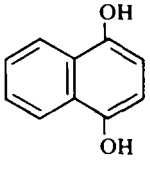

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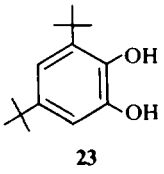

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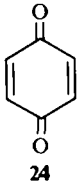

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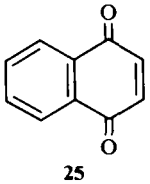

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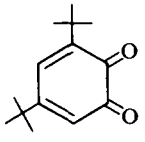

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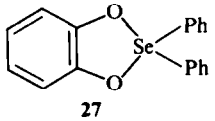

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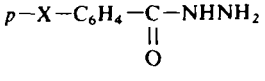
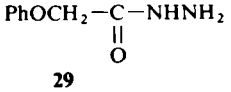


28 X = H
30 X = OMe
31 X = NO_2

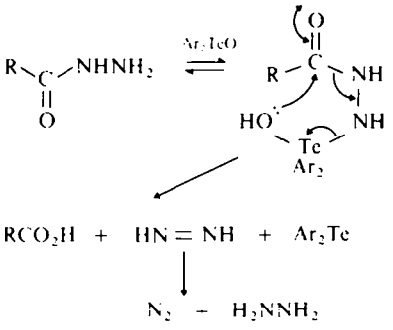


29

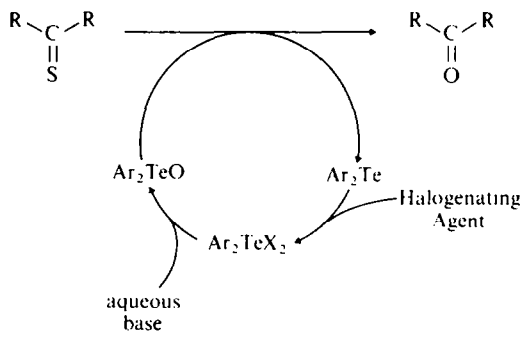
conditions of chromatography on silica gel a reverse reaction can take place (Scheme 4).

In order to further extend the scope of **1** as an oxidant we have studied its reaction with hydrazines as these oxidation reactions are of some interest.[16]

Thus reaction of the acyl hydrazines (**28** → **31**) with the telluroxide (**1**) gave the hydrazides (**32** → **35**) rapidly at room temperature. These reactions are therefore analogous to oxidation by diphenylselenoxide and benzeneseleninic anhydride. Of interest however was the additional isolation of *p*-anisic acid and *p*-nitrobenzoic acid, in low yield, from the oxidation of **30** and **31** respectively. A possible mechanism to account for these products is shown in Scheme (5). Treatment of the hydrazines (**36** → **40**) with **1** gave the parent arene, anisole and symmetrical and unsymmetrical diaryl tellurides (Table 2). The formation of the latter is interesting and deserves further study. We are not convinced that aryl radicals are involved.



Scheme 5



Scheme 6

Finally in this section the oxidation of hydrazine hydrate to diimide was attempted. Using only equivalent amounts of **1** and hydrazine hydrate in the presence of cinnammic acid (1.5 equiv) a fair amount of reduction did indeed occur, however, this potentially useful process was not investigated further.

In common with many other oxidising reagents the telluroxide (**1**) also rapidly converted N-phenylhydroxylamine into nitrosobenzene in high yield. Other examples of this oxidation were not studied.

Diazodiphenylmethane is of importance for the preparation of benzhydryl esters[17] and in heterocyclic synthesis[18] and is usually prepared by oxidation of benzophenone hydrazone.[19] Utilization of the telluroxide (**1**) as oxidant and subsequent trapping of the diazodiphenylmethane with *p*-anisic acid gave the corresponding benzhydryl ester in 77% yield.

In order to demonstrate the selectivity of the telluroxide (**1**) as an oxidant we find that it is inert to a wide variety of compounds many of which are often readily oxidised by other reagents. Those compounds which were found to be *unaffected* by **1** include, dithiolanes, enamines, aldehydes, ketones alcohols, pyrroles, indoles, amino acids, aromatic amines, mono hydroxylated aromatics, esters, hindered thiocarbamates, isonitriles, oximes, aryl hydrazones, sulphides and selenides. This impressive list we believe shows that **1** is therefore a mild and selective reagent.

Simple kinetic studies also reveal that **1** reacts approximately twice as fast with **23** than it does with **5b**, whereas the thiol (**19**) can be selectively oxidised in the presence of the catechol (**23**).

As catalytic oxidative processes are important in organic synthesis[20] we sought to establish such a process for various organotellurium species including **1**. Chosen for this study was the thiocarbonyl-carbonyl transformation for which a catalytic cycle can be represented as in Scheme 6. This cycle can obviously be entered at the telluride, telluroxide or tellurium dihalide stage and requires the telluride to be readily halogenated and subsequently converted to telluroxide by a suitable aqueous base.[4b]

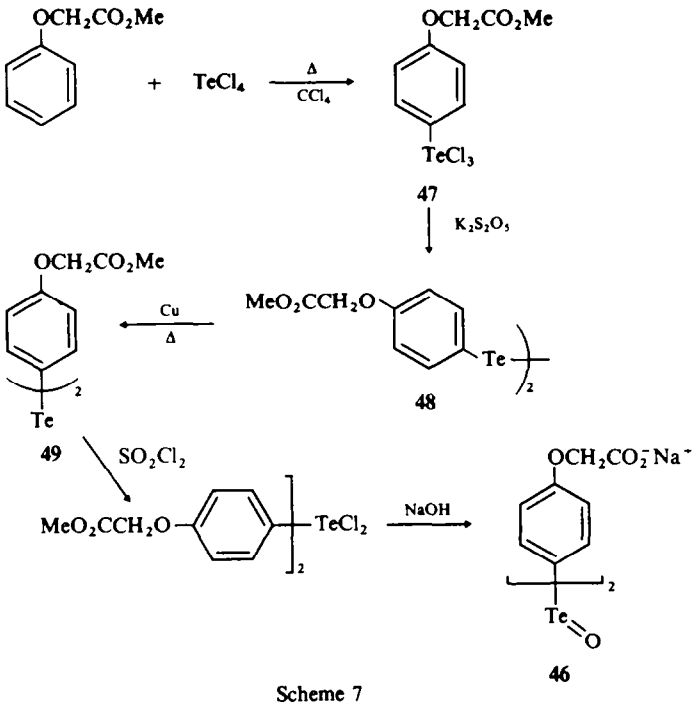
Although vicinal halides have been used before to effect halogenation of tellurides they often require high temperatures.[21] We found that the inexpensive 1,2-dibromotetrachloroethane was an excellent brominating[22] agent for tellurides at room temperature. Other reagents studied, hexachloroacetone, carbon tetrabromide, or Meldrum's acid dibromide were much less effective in the catalytic cycle. In control studies when equimolar amounts of the telluride (**3**) were mixed with the 1,2-dibromotetrachloroethane in light petroleum an 80% of the dibromide corresponding to **2** could be isolated.

In the catalytic cycle no oxidation took place in the absence of 1,2-dibromotetrachloroethane. For the reaction to work well aqueous potassium carbonate was the most satisfactory base although aqueous triethylamine could also be used.

Under optimum conditions the thiocarbonyl derivative is dissolved in chloroform together with 1.5% of the tellurium species. To this mixture was

Table 2. Oxidation of aryl hydrazines

Hydrazine Ar $NHNH_2$ Ar		PRODUCTS YIELD (%)		
		Arene ArH	Telluride R^1TeR^2 $R^1=R^2$=Anisyl (3)	R^1=Aryl R^2=Anisyl
Ph	(36)	53	68	29
4-MeC_6H_4	(37)	30	59	26
2,6-(DiMe)C_6H_3	(38)	70	74	5
4-BrC_6H_4	(39)	29	49	31
4-$HO_2CC_6H_4$	(40)	26	44	–

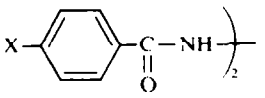


Scheme 7

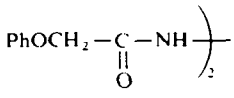
Table 3.* Oxidation of thiocarbonyl compounds at room temperature using 1,2-dibromotetrachloroethane as halogenating agent

Substrate	Eq. of halogenating agent	Eq. of tellurium species		Aqueous base	Time h	Yield %
5(a)	1.1	(3)	0.1	10%K_2CO_3	116	88
5(a)	3	(3)	0.1	10%K_2CO_3	23	90
5(a)	5	(3)	0.015	10%K_2CO_3	88	75
5(a)	5	(3)	0.015	20%K_2CO_3	20	70
5(a)	3	(3)	0.015	20%K_2CO_3	80	70
5(a)	5	(2)	0.1	20%K_2CO_3	26	87
5(a)	5	(3)	1	Et_3N	15	85
5(a)	5	(3)	0.1	Et_3N	48	41
5(a)	5	(41)	0.1	20%K_2CO_3	20	88
5(a)	5	(42)	0.1	20%K_2CO_3	2	88
5c	10	(3)	0.015	20%K_2CO_3	72	70
5c	5	(3)	0.015	20%K_2CO_3	114	70
8	5	(3)	0.015	20%K_2CO_3	72	60
13	5	(3)	0.015	20%K_2CO_3	15	Quant

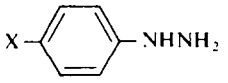
* In the absence of the tellurium species no reaction was observed.



32 X = H
34 X = OMe
35 X = NO_2

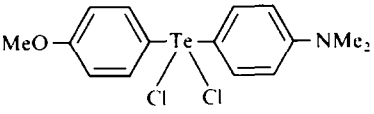


33

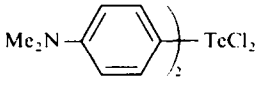


36 X = H
37 X = Me
39 X = Br
40 X = CO_2H

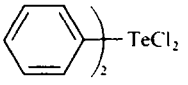
38



41



42



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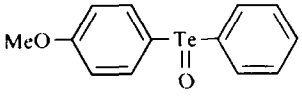
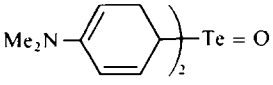


44



45

added an excess of 1,2-dibromotetrachloroethane and aqueous K_2CO_3 and the reaction mixture stirred vigorously until complete (Table 3).

Dipole moment studies have shown that there is appreciable mesomeric interaction of the ring π system with the Te atom in diaryl-tellurium compounds.[23] Also p_{Te}-π bonding is significant only when there are strong electron acceptor substituents on the rings. However, when powerful π-donor groups are present in the *para* positions of the rings the Te atom acts as a π-acceptor using its vacant 5d orbitals. It was therefore of interest to examine the effect of changing the aromatic substituents on the course and rate of the catalytic cycle. Thus in the table we have also compared other differently substituted dichlorides (**41**, **42** and **43**).

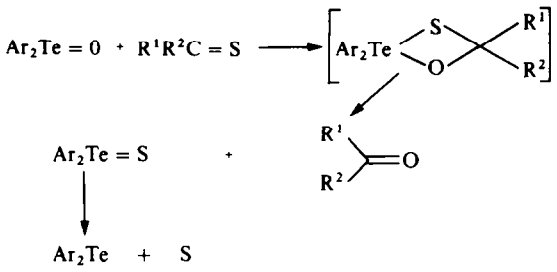
It appears that an increasing rate is observed in the series (**42** > **41** > **2** ≫ **43**). Although in separate experiments the telluroxide (**44**) reacted with the selenobenzoate (**4b**) to afford the corresponding benzoate after 1 h whereas **45** reacted with the dithiobenzoate (**5c**) at a similar rate to **1**.

In an effort to develop a potentially water soluble oxidant the telluroxide (**46**) was prepared in the following manner (Scheme 7).

Heating $TeCl_4$ in the presence of excess methylphenoxyacetate according to the method of Bergman[24] led to a very complicated mixture. However if the same reaction was repeated using carbon tetrachloride as solvent a 96% yield of the trichloride (**47**) was isolated. Treatment of **47** without further purification with potassium metabisulphite gave a 95% yield of the ditelluride (**48**). This compound was found to be unstable, tellurium being deposited on attempted crystallisation. When the crude ditelluride (**48**) was reacted with activated copper powder[25] in refluxing dioxan, a 98% yield of the telluride (**49**) was obtained which was readily crystallised from methanol. The telluroxide (**46**) was subsequently obtained by treatment of **49** with sulphuryl chloride in dry benzene followed by aqueous sodium hydroxide. Isolation of **46** was achieved by precipitation with acetone.

Preliminary results using **46** as a water soluble oxidant do not suggest that it will be very effective for transformations discussed above.

However we have shown that dianisyl telluroxide is a useful new mild, selective oxidising reagent which can be used in a catalytic cycle. We anticipate further synthetic uses of some of the Te^{IV} species described.



Scheme 8

We have not studied the mechanism of the conversion of thiocarbonyl or selenocarbonyl compounds into their carbonyl analogues. However, we made the first experiments with the idea (for thiocarbonyl derivatives) summarised in Scheme 8. Although this proposal is naive it would seem to merit further consideration.

EXPERIMENTAL

M.ps were determined using a Kofler hot stage apparatus and are uncorrected. IR spectra were recorded on Perkin–Elmer 197 and 298 spectrometers, NMR spectra were recorded using a Varian EM 360 machine. Mass spectra were recorded on a V.G. Micromass 7070 spectrometer. Solvents were purified and dried by standard techniques.

Preparation of 4,4'-dimethoxydiphenyltelluroxide (**1**). 4,4'-Dimethoxydiphenyltellurium dichloride[24] (8.00 g) was stirred at 95° in NaOH aq (100 ml, 5%) for 1 hr. After cooling to 0° the white solid was filtered off, washed with cold water (3 × 10 ml), and dried under vacuum over P_2O_5 to give **1** (5.60 g 81%), m.p. 187–189° (lit.[26], 190–191°), ν_{max} (Nujol) 1585, 1575, 1490, 1460, 1401, 1380, 1295, 1247, 1180, 1172, 1109, 1068, 1026, 823, 811, and 789 cm^{-1}, δ 7.70 (4 H, d, J 9 Hz), 6.78 (4 H, d, J 9 Hz), and 3.78 (6 H, s), *m/e* 360 (M^+ absent), 344, 214 (100%), and 199.

Oxidation of triphenylphosphine. Triphenylphosphine (262 mg) and **1** (358 mg) were dissolved in $CHCl_3$ (4 ml) (N_2). After 48 hr the $CHCl_3$ was removed under reduced pressure and the residue subjected to column chromatography (benzene–EtOAc 9 + 1) to give **3** (261 mg, 73%) and triphenylphosphine oxide (223 mg, 80%), m.p. 153–157° (lit.[27], m.p. 154–157°).

Oxidation of tri-n-butylphosphine. Tri-n-butylphosphine (133 mg) and **1** (236 mg) were dissolved in $CHCl_3$ (4 ml) (N_2). After 0.5 hr the $CHCl_3$ was removed under reduced pressure and column chromatography (EtOAc) of the residue gave **3** (161 mg, 71%) and tri-n-butylphosphine oxide (140 mg, 97%) as a colourless oil δ 1.60 (broad m) and 0.90 (broad m), *m/e* 218 (M^+), 189, 162, 161, 147, 134, 120 (100%), and 92.

General procedure for the oxidation. All the reactions were performed at room temp under N_2 in either $CHCl_3$ or CH_2Cl_2. Approximately 10 ml of solvent was used for every 100 mg of substrate. For thiocarbonyl derivatives 1·1 equiv of **1** was used, for thiols 0·55 equiv. The mixtures were concentrated by partial evaporation of the solvent and subjected to plc or column chromatography to isolate the products. The product yields refer to chromatographic yields unless otherwise specified. The telluride (**3**) was always recovered in yields ranging from 64–96% while S (or Se) were always recovered in near quantitative yields from the reactions with thiocarbonyl derivatives.

Oxidation of xanthate (**4a**). Compound **4a** (116 mg) after 24 hr afforded 5α-cholestan-3β-ol-methylthiocarbonate (114 mg, 100%) m.p. 117–119. Crystallisation from EtOAc gave (80 mg, 72%) m.p. 119.5–120.5° (lit.[28], 117°), ν_{max} ($CHCl_3$) 1700 cm^{-1}, *m/e* 462 (M^+, weak), 371, 355, 258, 256 (100%), 192, 160 and 128.

Oxidation of selenobenzoate (**4b**). Compound **4b** (278 mg) after 0.3 hr afforded 5α-cholesten-3β-ol-benzoate (229 mg, 93%). Crystallisation from EtOAc gave (198 mg, 80%), m.p. 136–137° (lit.[29a], 136–137°).

Oxidation of thionbenzoate (**5a**). Compound **5a** (253 mg) after 1.5 hr afforded 5-cholestan-3β-ol-benzoate (162 mg, 66%) m.p. 143–145°. Crystallisation from EtOAc gave (130 mg, 53%), m.p. 144–145.5° (lit.[29b], 150–151°), ν_{max} (CCl_4) 1722 cm^{-1}.

Oxidation of thionacetate (**5b**). Compound **5b** (111 mg) after 0.25 hr afforded 5-cholesten-3β-ol-acetate (107 mg, 100%). Crystallisation from acetone gave (90 mg, 84%), m.p. 113–114° (lit.[29b], m.p. 114–115°).

Oxidation of dithiobenzoate (**5c**). Compound **5c** (130 mg) after 27 hr afforded 5-cholesten-3β-thiol-benzoate (88 mg, 70%), m.p. 160–162°. Crystallisation from EtOAc gave (65 mg; 52%), m.p. 164.5–166° (lit.[28], 167°), m/e 506 (M^+, weak), 369, and 368 (100%).

Oxidation of thiourea (**6a**). Compound **6a** (38 mg) after 16 hr (MeOH as solvent) afforded urea (22 mg, 73%), ν_{max} (Nujol) 1660 (broad) cm^{-1}.

Compound **6a** (38 mg) after 63 hr (water as solvent), extraction of the aqueous phase with CH_2Cl_2 and evaporation of the water at room temp under reduced pressure afforded urea (34 mg, 100%).

Oxidation of 1,3-diphenylthiourea (**6b**). Compound **6b** (114 mg) after 16 hr (MeOH as solvent), evaporation of the MeOH under reduced pressure, trituration of the residue with benzene, and filtration afforded 1,3-diphenylurea (72 mg, 68%), m.p. 234° (lit.[29c], 238–239°), *m/e* 212 (M^+), 119, 93 (100%), 77, 66 and 65.

Oxidation of thioncarbonate (**7**). Compound **7** (145 mg) after 0.5 hr afforded the corresponding carbonate (132 mg, 96%), m.p. 145–147° (lit.[30], 147°), *m/e* 273 ($M^+ - 15$) and 101 (100%).

Oxidation of trithiocarbonate (**8**). Compound **8** (95 mg) after 20 hr afforded S (16 mg, 100%) and a mixture of **3** and cyclohexan-1,2-*trans*-diyldithiocarbonate (228 mg), ν_{max} ($CHCl_3$, mixture) 1730 and 1640 cm^{-1}, (mixture) 7.58 (4 H, d, J 8 Hz), 6.70 (4 H, d, J 8 Hz), 3.75 (8 H, overlapping s and m), and 2.30–1.25 (8 H, m).

Oxidation of thionbenzoate (**9**). Compound **9** (97 mg) after 4 hr afforded n-octadecanylbenzoate (85 mg, 91%), m.p. 41–42°, *m/e* 374 (M^+), 253, 252, 224, 123 (100%), 105 and 97.

Oxidation of xanthate (**10**). Compound **10** (118 mg) after 1 hr afforded ergosteryl-3β-ol-methylthiocarbonate (111 mg, 98%), m.p. 124° (lit.[28], 125°), ν_{max} ($CHCl_3$) 1700 cm^{-1}.

Oxidation of xanthate (**11**). Compound **11** (118 mg) after 0.75 hr afforded 3-O-(methylthiocarbonyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (98 mg, 87%), m.p. 76–78°, *m/e* 319 ($M^+ - 15$), 261, 201, 195, 113, 101 (100%), and 75.

Oxidation of thiofenchone (**12**). Compound **12** (23 mg) after 42 hr afforded fenchone (5 mg, 23%), ν_{max} (Neat) 1965, 1930, 1875, 1742, 1465, 1385, and 1025 cm^{-1}, S (3 mg, 75%) and **3** (39 mg, 81%). The low yield of fenchone is caused by its volatility.

Oxidation of di-t-Butylthioketone (**13**). Compound **13** (197 mg) after 0.3 hr showed (glc) a quantitative conversion into di-t-butylketone, ν_{max} 1680 cm^{-1}. Plc (petroleum–ethyl acetate 9 + 1) afforded S (36 mg, 90%) and **3** (330 mg, 96%).

Oxidation of thiopiperidone (**14**). Compound **14** (115 mg) after 20 hr afforded 2-piperidone (86 mg, 87%) as a colourless oil, ν_{max} (Neat) 3400–3250 and 1650 cm^{-1} identical to an authentic sample.

Oxidation of thiocamphor (**15**). Compound **15** (168 mg) after 2 hr afforded a mixture of **2** and camphor (10% by glc) plus a non-polar product which appeared to be a diastereomeric mixture of *bis*-vinyldisulphides (116 mg, 70%) which slowly converted on standing to **16**, m.p. 174–177° (lit.[9], 173–174° for an optically pure sample), δ 2.50 and 2.33 (s and distored d, integral ratio 1:1) and 2.2–0.6 (m). No S could be isolated.

Oxidation of phenylisothiocyanate. Phenylisothiocyanate (121 mg) after 0.25 hr afforded 1,3-diphenylurea (50 mg, 52%) m.p. 236–238° (lit.[29c], 238–239°), *m/e* 212 (M^+), 119, 93 (100%), 77, 66, and 65.

Oxidation of L-cysteine hydrochloride (**17**). L-Cysteine hydrochloride (**17**) (157 mg), **1** (197 mg) and NaOAc (82 mg) were stirred at room temp under N_2 in de-oxygenated water (7 ml) for 1.5 hr. The heterogeneous mixture was filtered, the insoluble white solid washed with water (2 × 2 ml), EtOH (2 × 2 ml) and finally $CHCl_3$ (4 × 2 ml) to afford L-cystine (95 mg, 79%), m.p. 260° dec (lit.,[29c] 258 261° dec), ν_{max} (KBr) 2900 broad, 2030, 1620 shoulder, 1580 broad, 1470, 1400, 1380, 1335, 1295, 1190, 1120, 1085, 1035, 960, 875, 850, 780, and 680 cm^{-1}. The filtrate was *evaporated under reduced pressure*: column chromatography of the residue afforded **3** (121 mg, 68%).

Oxidation of thiobenzyl alcohol (**18**). Compound **18** (0.10 ml) after 0.5 hr afforded **2** (84 mg, 58%) and dibenzyldisulphide (100 mg, 96%). Crystallisation from EtOH gave **2** (80 mg, 77%) m.p. 68.5–70° (lit.,[29c] 71 72° and 69–70°), δ 7.27 (10 H, s) and 3.57 (4 H, s).

Oxidation of p-thiocresol (**19**). Compound **19** (246 mg) after 0.1 hr afforded **3** (270 mg, 76%) and di-*p*-tolyldisulphide (239 mg, 98%) m.p. 44–45°. Recrystallised from EtOH gave **3** (202 mg, 83%) m.p. 47 47.5° (lit.,[29f] 48°), δ 7.37 (4 H, d, J 8 Hz), 7.05 (4 H, d, J 8 Hz), and 2.30 (6 H, s).

Oxidation of p-aminothiophenol (**20**). Compound **20** (200 mg) after 1 hr afforded **2** (246 mg, 85%) and 4,4'-diaminodiphenyldisulphide (114 mg, 58%), m.p. 73.5 75° (lit.,[29g] 85 and 106°), δ 7 77 (4 H, d, J 8 Hz), 6.57 (4 H, d, J 8 Hz), and 3.67 (4 H, broad s).

Oxidation of 1,4-dihydroxybenzene (**21**). Compound **21** (55 mg) and **1** (196 mg) were dissolved in $CHCl_3$ (2 ml) at ambient temp under N_2. After 0.25 hr the mixture was subjected to plc to afford **3** (8 mg, 5%) and **24** (35 mg, 65%), m.p. 114 115° (lit.,[29h] 115.7°).

Oxidation of 1,4-dihydroxynapthalene (**22**). Similarly **22** (80 mg) with **1** (196 mg) in $CHCl_3$ (2 ml) gave the telluride (96 mg, 56%) and **25** (77 mg, 97%). m.p. 122–125° which on recrystallisation (EtOH) gave yellow needles (60 mg, 76%) m.p. 125–126° (lit.,[29h] 126°), δ 8.27 7.67 (4 H, m) and 7.00 (2 H, s).

Oxidation of 2,4-Di-t-butylcatechol (**23**). Similarly **23** (111 mg) with **1** (358 mg) in $CHCl_3$ (4 ml) afforded **26** (88 mg, 80%) as a deep red crystalline solid, m.p. 112–114° (lit.,[31] 113 114°), δ 6.92 (1 H, d, J 2 Hz), 6.18 (1 H, d, J 2 Hz), 1.29 and 1.23 (both s, combined integral 18 H). No **3** was isolated.

Oxidation of **28**. Compound **28** (68 mg) and **1** (188 mg) were dissolved in CH_2Cl_2 (3 ml) at ambient temp under N_2. After 1 hr the mixture was filtered, the ppt washed with CH_2Cl_2 (2 × 2 ml) and the filtrate evaporated under reduced pressure to yield a red oil. Column chromatography of this oil afforded **3** (151 mg, 85%). The white ppt, after drying under vacuum afforded *sym*-**32** (35 mg, 58%), m.p. 242 243° (lit.,[32] 241°), *m/e* 240 (M^+), 222, 105 (100%), and 77.

Oxidation of **29**. Compound **29** (166 mg) with **1** (376 mg) in $CHCl_3$ (4 ml) after 24 hr afforded *sym*-**33** (90 mg, 67%), m.p. 165–167°, *m/e* 300 (M^+), 179, 151, 147, 133, 118, 107, 104 (100%), and 77.

Oxidation of **30**. Compound **30** (166 mg) with **1** (376 mg) as above afforded **3** (315 mg, 92%), *p*-anisic acid (9 mg, 6%) and *sym*-**34** (120 mg, 86%) m.p. 150–168°, *m/e* 300 (M^+).

Oxidation of **31**. Compound **31** (181 mg) with **1** (386 mg) afforded the telluride (312 mg, 91%), *p*-nitrobenzoic acid (40 mg, 24%), and *sym*-**35** (100 mg, 67%), m.p 187–194°.

General procedure for the oxidation of phenylhydrazines (**36–40**). The reactions were performed at room temp with 1.1 equivs of **1** under N_2 in CH_2Cl_2, 2 ml of solvent being used for every 0.50 mmol phenylhydrazine. N_2 was always evolved with 82% of the theoretical amount being measured in the oxidation of phenylhydrazine (**36**). The crude mixtures were analysed by glc (2 m, column, 1/8" o.d., 10% OV-17 on Chromosorb using a gradient temp programme) for aromatic hydrocarbons and anisole. The amounts of aromatic hydrocarbons produced were estimated by comparing peak areas to those of standard solns of benzene, toluene, *m*-xylene and bromobenzene. The mixtures were then subjected to plc to isolate the organo-tellurium products.

Oxidation of phenylhydrazine (**36**). Compound **36** (121 mg) after 0.2 hr gave benzene (53%) **3** (262 mg, 68%) and *phenyl-p-methoxylphenyl-telluride* (101 mg, 29%), m.p. 61–62° (from MeOH) (lit.,[33] 60.5–61.5), δ 7.63 (d, J 8 Hz), 7.72–7.00 (m), 6.70 (d, J 8 Hz), combined intregral 9 H, and 3.73 (3 H, s), *m/e* 314 (M^+), 184 (100%), 168, 141, and 77 (Found: C, 50.03; H, 3.86. Calc for $C_{13}H_{12}OTe$: C, 50.07; H, 3.88%).

Oxidation of p-*tolylhydrazine* (**37**). Compound **37** (61 mg) after 0.2 hr gave toluene (30%), **3** (102 mg, 59%) and *p-methyl-p-methoxydiphenyltelluride* (43 mg, 26%), m.p. 65.5 67° (from MeOH) (lit.,[34] 64–64.5), δ 7.67 and 7.47 (both d, J 9 Hz, combined integral 4 H), 6.93 and 6.70 (both d, J 9 Hz, combined ontegral 4 H), 3.77 (3 H, s), and 2.30 (3 H, s), *m/e* 328 (M^+), 210, 198 (100%), 183, 145, 91, 77, and 65 (Found: C, 51.62; H, 4.31. Calc. for $C_{14}H_{14}OTe$: C, 51.60; H, 4.33%).

Oxidation of 2,6-dimethylphenylhydrazine (**38**). Compound **38** (68 mg) after 0.2 hr gave *m*-xylene (70%), **3** (126 mg, 74%) and what appears to be 2,6-dimethylphenyl-4-methoxyphenyltelluride (9 mg, 5%) as a colourless oil, *m/e* 342 (M^+, 100%), 234, 212, 197, 105, 104, 79, and 77.

Oxidation of p-bromophenylhydrazine (**39**). Compound **39** (187 mg) after 2.5 hr gave bromobenzene (29%), **3** (166 mg, 49%) and p-*bromo*-p'-*methoxydiphenyltelluride* (120 mg, 31%), m.p. 55.5 57 (MeOH), δ 7.64 (2 H, d, J 9 Hz), 7.43–7.13 (2 H, m), 6.71 (2 H, d, J 9 Hz), and 3.76 (3 H, s), *m/e* 394 (M^+), 264 + 262 (100%), 249/247, 237/235, 222, and 92 (Found: C, 39.99; H, 2.80. Calc. for $C_{13}H_{11}BrOTe$: C, 39.96; H, 2.84%).

Oxidation of p-hydrazinobenzoic acid (**40**). Compound **40** (152 mg) with **1** (394 mg) after 24 hr was poured into sat. K_2CO_3 aq, the phases separated and the aqueous phase extracted with CH_2Cl_2 (2 × 10 ml). The combined organic phases were dried over $NaSO_4$ and evaporated under reduced pressure. The residue afforded **3** (151 mg, 44%). The aqueous phase, on acidification with HCl and extraction with CH_2Cl_2 gave a yellow solid (54 mg) which on sublimation gave benzoic acid (32 mg, 26%), m.p. 122° (lit.,[28] 122°).

Oxidation of phenylhydroxylamine. Phenylhydroxylamine (109 mg) with the **1** (376 mg) in $CHCl_3$ (4 ml) at room temp for 0.1 hr gave **3** (150 mg, 88%) and nitrosobenzene (96 mg, 90%), m.p. 66–67 (lit.,[29k] 67.5 68°).

Oxidation of benzophenone hydrazone. Benzophenone hydrazone (98 mg, 0.50 mmol) and **1** (197 mg, 0.55 mmol) were stirred in $CHCl_3$ (4 ml) for 22 hr. *p*-Anisic acid (152 mg, 1 mmol) was added to the deep red soln which was briefly heated to reflux and allowed to stir at room temp for 1 hr afforded the benzhydryl ester of *p*-anisic acid (122 mg, 77%), m.p. 95–96 (lit.,[17] 96), *m/e* 318 (M^+), 182, 167 (100%), 166, 165, 135, 105, 91, and 77.

Preparation of 1,2-dibromotetrachloroethane. A stirred soln of tetrachloroethylene (10.22 ml) and Br_2 (2.58 ml) in CCl_4 (50 ml) was irradiated with a 500W lamp for 16 hr. The solvent was removed under reduced pressure to leave a white solid (24.55, 100%), m.p. 104 softening from 95°.

Bromination of dianisyltelluride (**3**) *using 1,2-dibromotetrachloroethane.* Compound **3** (70 mg) and 1,2-dibromotetrachloroethane (67 mg) were stirred in petroleum for 16 hr. Filtration of the pale yellow solid and washing with petroleum (2 × 2 ml) gave 4,4'-dimethoxydiphenyl tellurium dibromide (82 mg, 80%). The solid was recrystallised (chloroform/petroleum) to afford yellow needles, m.p. 192–200 (lit.,[35] 198), δ 7.95 (4 H, d, J 9 Hz), 6.92 (4 H, d, J 9 Hz), and 3.83 (6 H, s).

General procedure for the catalytic oxidation of thiocarbonyl compounds (**5a**, **8**, *and* **5c** *using* 1,2-*dibromotetrachloroethane as brominating agent.* The thiocarbonyl compound was stirred in a two phase system of CH_2Cl_2 or $CHCl_3$ and aqueous base (K_2CO_3 or Et_3N) containing an excess of the dibromide and varying amounts of dianisyltellurium compound (dianisyltelluride or dianisyl tellurium dichloride). On completion of the reaction (plc petroleum to elute unreacted dibromide followed by petroleum-EtOAc 20 + 1) the phases were separated and the aqueous phase extracted with CH_2Cl_2 (2 × 2 ml). The combined CH_2Cl_2

extracts were dried over $NaSO_4$ and the solvent evaporated under reduced pressure. Column chromatography (petroleum followed by petroleum-EtOAc 20 + 1) gave unreacted dibromide and oxo-derivative. The molar proportions of reactants, quantities of solvents, reaction times and product yields are given below:

(a) **5a** (0.49 mmol), dibromide (0.53 mmol), **3** (0.05 mmol), CH_2Cl_2 (5 ml), 10% K_2CO_3 aq (5 ml), 116 hr, cholesteryl benzoate (0.42 mmol, 88%).

(b) **5a** (0.40 mmol), dibromide (1.18 mmol), **3** (0.04 mmol), CH_2Cl_2 (5 ml), 10% K_2CO_3 aq (5 ml), 23 hr, cholesteryl benzoate (0.36 mmol, 90%).

(c) **5a** (0.40 mmol), dibromide (1.98 mmol), **3** (0.006 mmol), $CHCl_3$ (2 ml), 10% K_2CO_3 aq (5 ml), 88 hr, cholesteryl benzoate (0.30 mmol, 74%).

(d) **5a** (0.40 mmol), dibromide (2.01 mmol), **3** (0.006 mmol), $CHCl_3$ (2 ml), 20% K_2CO_3 aq (5 ml), 20 hr, cholesteryl benzoate (0.29 mmol, 70%).

(e) **5a** (0.40 mmol), dibromide (1.18 mmol), **3** (0.006 mmol), $CHCl_3$ (2 ml), 20% K_2CO_3 aq (5 ml), 80 hr, cholesteryl benzoate (0.29 mmol, 70%).

(f) **5a** (0.20 mmol), dibromide (1.00 mmol), dianisyl tellurium dichloride (0.02 mmol), $CHCl_3$ (2 ml), 20% K_2CO_3 aq (2.5 ml), 26 hr, cholesteryl benzoate (0.17 mmol, 87%).

(g) **5a** (0.20 mmol), dibromide (1.00 mmol), **2** (0.20 mmol), $CHCl_3$ (2 ml), Et_3N (1.00 mmol) in water (3 ml), 15 hr, cholesteryl benzoate (0.17 mmol, 85%).

(h) **5a** (0.20 mmol), dibromide (1.00 mmol), **2** (0.002 mmol), $CHCl_3$ (2 ml), Et_3N (1.00 mmol) in water (0.50 ml), 48 hr, cholesteryl benzoate (0.08 mmol, 41%), and **4a** (0.07 mmol, 36%).

(i) **8** (0.40 mmol), dibromide (2.00 mmol), **2** (0.006 mmol), $CHCl_3$ (2 ml), 20% K_2CO_3 aq (5 ml), 72 hr, cyclohexan-1,2-*trans*-diyl-dithiocarbonate (0.24 mmol, 60%).

(j) **5c** (0.40 mmol), dibromide (4.00 mmol), **2** (0.006 mmol), $CHCl_3$ (2 ml), 20% K_2CO_3 aq (5 ml), 72 hr, 5-cholesten-3β-thiol-benzoate (0.28 mmol, 70%).

(k) **5c** (0.40 mmol), dibromide (2.00 mmol), **2** (0.006 mmol), $CHCl_3$ (2 ml), 20% K_2CO_3 aq (5 ml), 15 hr, 5-cholesten-3β-thiol-benzoate (0.28 mmol, 70%).

Oxidation of di-t-butylthioketone (**13**). Compound **13** (63 mg), dibromide (654 mg), and **3** (2 mg) were stirred in a two phase system of $CHCl_3$ (2 ml) and K_2CO_3 aq (5 ml, 20%) for 15 hr. After this time the colour of the thioketone had been completely quenched. The phases were separated, the $CHCl_3$ phase dried over $MgSO_4$ and an IR spectrum of the crude $CHCl_3$ solution showed a strong band at 1683 cm^{-1} due to di-t-butylketone.

General procedure for the oxidation of thionbenzoate (*5a*) *using catalytic amounts of* **2**,[24] **42**,[36] **41**[37] and **43**.[38] Compound **5a** (0.20 mmol), diaryl tellurium dichloride (0.02 mmol), and 1,2-dibromotetrachloroethane (1.0 mmol) were stirred at room temp in a two phase system of $CHCl_3$ (2 ml) and K_2CO_3 (2.5 ml, 20%). The reaction times and yields of cholesteryl benzoate (where determined) are given below:

(a) Using **2** after 46 hr gave a 47% benzoate.

(b) Using **42** after 2 hr gave an 88% yield of benzoate.

(c) Using **41** after 20 hr gave an 88% yield of benzoate.

(d) Using diphenyl tellurium dichloride showed a trace of starting **5a** even after 92 hr.

Preparation of 4-methoxy-4'-N,N-dimethylaminodiphenyltelluroxide (**44**). 5-Methoxyphenyl tellurium trichloride[35] (2.00 g) and N,N-dimethylaniline (1.65 ml) were stirred together at room temp in a stoppered flask. The mixture rapidly became very viscous and the minimum amount of $CHCl_3$ was added to ensure adequate stirring. After 16 hr the reaction was filtered, the residue washed with ether (3 × 5 ml) and MeOH (3 × 5 ml) and dried under vacuum to afford **41** (1.22 g, 49%). Recrystallisation from MeOH gave yellow needles, m.p. 167–169° (lit.,[37] m.p. 170–172°), δ 7.86 and 7.73 (4 H, both d, J 9 Hz), 6.90 (2 H, d, J 9 Hz), 6.62 (2 H, d, J 9 Hz), 3.78 (3 H, s), and 3.00 (6 H, s), *m/e* 357 ($M^+ - Cl_2$), 344, 272, 254 (100%), 237, 227 and 212 (Found: C, 42.24; H, 4.04; N, 3.07; Cl, 16.43. Calc. for $C_{15}H_{17}NOTeCl_2$: C, 42.31; H, 4.02; N, 3.29; Cl, 16.55%).

The above dichloride **41** (1.22 g) was stirred in NaOHaC (20 ml, 5%) at 80° for 0.75 hr. The reaction was cooled in an ice bath, filtered, the insoluble white solid washed with water (3 × 5 ml), and dried under vacuum over P_2O_5 to afford **44** (0.886 g, 84%), m.p. 209–210.5°, δ 7.64 and 7.56 (4 H, both d, J 9 Hz), 6.93 (2 H, d, J 9 Hz), 6.69§2 H, d, J 9 Hz), 3.80 (3 H, s), and 2.99 (6 H, s).

Reaction of telluroxide (**44**) *with selenobenzoate* (**4b**). Compound **44** (102 mg) and **3b** (139 mg) were dissolved in $CHCl_3$ (2 ml) and stirred at room temp for 1 hr under a N_2. Filtration gave Se (18 mg, 90%) and plc (petroleum-EtOAc 9 + 1) afforded 5-α-cholestan-3β-ol benzoate (120 mg, 97%) and *4-methoxy-4'-N,N-dimethylaminodiphenyltelluride* (88 mg, 99%). Recrystallisation of the telluride from MeOH gave a colourless solid, m.p. 97–98°, δ 7.62 and 7.53 (4 H, both d, J 9 Hz), 6.68 and 6.53 (4 H, overlapping d, J 9 Hz), 3.72 (3 H, s) and 2.92 (6 H, s), *m/e* 357 (M^+), 250, 227 (100%), 212 and 113 (Found: C, 50.95; H, 4.87; N, 3.78. Calc. for $C_{15}H_{17}NOTe$: C, 50.76; H, 4.83; N, 3.95%).

Preparation of 4,4'-tetramethyldiaminodiphenyltelluroxide (**45**). 4,4'-Tetramethyldiaminodiphenyltellurium dichloride was prepared as described in the lit.[36] The dichloride (800 mg) was refluxed in NaOH aq (1.0 M, 10 ml) for 0.1 hr, cooled in an ice bath and filtered. The insoluble white solid was washed with cold water (2 × 5 ml) and dried under vacuum to afford **45** (570 mg, 81%), m.p. 225–227.5°, δ 7.54 (4 H, d, J 9 Hz), 6.73 (4 H, d, J 9 Hz) and 2.99 (12 H, s), *m/e* 370 ($M^+ - 16$), 240 (100%), 225 and 120.

Oxidation of dithiobenzoate (**5c**) *using telluroxide* (**45**). Compound **5c** (122 mg) and **45** (100 mg) were stirred in $CHCl_3$ (3 ml) for 27 hr (N_2). Plc (petroleum–EtOAc 19 + 1) afforded 5-cholesten-3β-thiol-benzoate (77 mg, 65%). Material which was assumed to be the tetramethyldiaminotelluride decomposed rapidly on the chromatographic plate.

Preparation of 4-(methyl phenoxyacetate) tellurium trichloride (**47**). Tellurium tetrachloride (11.4 g) and methyl phenoxyacetate (21.0 g) were refluxed in CCl_4 (175 ml) for 18 hr. The reaction was cooled in an ice bath and filtered to give the crude **47** (16.1 g, 96%) which was used in the following reaction without further purification.

Preparation of 4,4'-ditelluro-bis-(methyl phenoxyacetate) (**48**). Compound **47** (16.0 g) was stirred in a two phase system of CH_2Cl_2 (200 ml) and water (200 ml). $KHSO_3$ (4 g) was added in small portions over a period of 0.1 hr and the reaction stirred for a further 1 hr at room temp. The phases were separated, the aqueous phase extracted with CH_2Cl_2 and the combined organic extracts dried over $MgSO_4$. Filtration and evaporation of the solvent under reduced pressure gave **48** as a red oil which slowly solidified (11.1 g, 95%), m.p. 68–74°, δ 7.67 (4 H, d, J 0 Hz), 6.70 (4 H, d, J 9 Hz), 4.55 (4 H, s), and 3.77 (6 H, s), *m/e* 590 (M^+), 460 (M^+–Te), 295, 257, 166 and 79 (100%). This was used without further purification in the following step.

Preparation of 4,4'-telluro-bis-(methyl phenoxyacetate (**49**). Compound **48** (1.90 g) and activated Cu powder[25] (0.62 g) were refluxed in dry dioxan (50 ml) for 2 hr under N_2. The reaction was filtered to remove a small amount of Te. Evaporation of the filtrate and column chromatography of the residue afforded *4,4'-telluro-bis-(methyl phenoxyacetate)* (**49**) (1.46 g, 98%), m.p. 108–109° (from MeOH), ν_{max} ($CHCl_3$) 2958, 1760, 1740 (shoulder), 1585, 1570, 1485, 1440, 1294, 1175 and 1085 cm^{-1}, δ 7.55 (4 H, d, J 9 Hz), 6.78 (4 H, d, J 9 Hz), 4.56 (4 H, s), and 3.76 (6 H, s) (Found: C, 47.24; H, 3.90. Calc. for $C_{18}H_{18}O_6Te$: C, 47.21; H, 3.96%).

Formation of the telluroxide (**46**). Compound **49** (2.67 g) was dissolved in benzene (80 ml) and treated with sulphuryl chloride (0.52 ml). After 0.5 hr the benzene was evaporated under reduced pressure to leave a sticky, white solid which defied all attempts at recrystallisation, ν_{max} (Film) 1756, 1584, 1575 (shoulder), 1490, 1438, 1215, 1180, 1076, 822, and 755, δ 7.96 (4 H, d, J 9 Hz), 6.95 (4 H, d, J 9 Hz), 4.83 (4 H, s), and 3.80 (6 H, s).

Cl, 16.43. Calc. for $C_{15}H_{17}NOTeCl_2$: C, 42.31; H, 4.02; N, 3.29; Cl, 16.65%).

The above dichloride **41** (1.22 g) was stirred in NaOH aq (20 ml, 5%) at 80° for 0.75 hr. The reaction was cooled in an under vacuum afforded **46** (2.88 g, 100%), m.p. 310°, ν_{max} (Nujol) 3520, 3400 3080 (broad), 1625, 1610, 1590, 1486, 1435, 1425, 1336, 1285, 1200, 1184, 1055, 830, and 820 cm^{-1}, δ (D_2O/external TMS) 7.62 (4 H, d, J 0Hz), 7.03 (4 H, d, J 9 Hz), and 4.48 (4 H, s).

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