Bis(*p*-methoxyphenyl) Telluroxide: a New, Mild Oxidising Agent

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Summary Bis(*p*-methoxyphenyl) telluroxide is a mild and highly selective oxidising reagent for the conversion of thiocarbonyl groups into their oxo analogues and thiols into disulphides, and for the oxidation of a limited number of nitrogenous compounds although many other easily oxidised functions are not affected.

Bis(*p*-methoxyphenyl) telluroxide (**1**), which is easily prepared by basic hydrolysis of the corresponding diaryltellurium dichloride,[1] is odourless and readily soluble in organic solvents. Its oxidising properties, however, have not been previously investigated.

Table 1. Oxidation of thiocarbonyl and thiol compounds.[a]

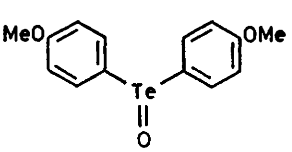
Compound	Reaction time/h	Yield of oxo derivative (or disulphide)/%	Compound	Reaction time/h	Yield of oxo derivative (or disulphide)/%
(**2a**)	0·25	Quant.	(**4b**)	16	68[c]
(**2b**)	27	70	(**5**)	0·1	(98)[b]
(**2c**)	1·5	66	(**6**)	0·5	(96)[b]
(**3a**)	24	Quant.	(**7**)	1·5	(79)[b,e]
(**3b**)	0·3	93	(**8**)	0·3	Quant.[f]
(**4a**)	16	73[c]	(**12**)	0·25	52[g]
	63	Quant.[d]			

[a] Reactions carried out at room temperature in chloroform with 1·1 equiv. of telluroxide. [b] With 0·55 equiv. of telluroxide. [c] Methanol as solvent. [d] Water as solvent. [e] Aqueous sodium acetate as solvent and isolated by precipitation. [f] Yield determined by g.l.c. [g] Yield of hydrolysis product, 1,2-diphenylurea.

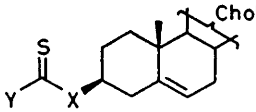
Here we show its use as a mild and highly selective reagent for the conversion of xanthates, thiocarbonates, thioamides, and thiones into their corresponding oxo derivatives and of thiols into disulphides (Table 1). The reactions were carried out under nitrogen in a suitable solvent (usually chloroform or dichloromethane) at room temperature and monitored by t.l.c. where possible. The products were isolated by preparative-layer or column chromatography. The by-products which were readily isolated from the reactions were sulphur from the thione conversions and always bis(*p*-methoxyphenyl) telluride which could be reoxidised to (**1**).

In the oxidation of L-cysteine hydrochloride (**7**), the solvent (water) was thoroughly deoxygenated with nitrogen and the isolation of bis(*p*-methoxyphenyl) telluride in a 68% yield confirmed that aerial oxidation had not taken place.

The thiones (**8**) and (**9**) both reacted rapidly with (**1**) but the volatility of the products prevented an accurate isolated yield from being determined. However, g.l.c. analysis showed a quantitative conversion of (**8**) into di-t-butyl ketone while in both cases sulphur and telluride were isolated in near quantitative yields. The enolisable thiocamphor (**10**) gave a mixture of products, two of these being the divinyl disulphide (**11**), isolated in a 67% yield, and camphor present to the extent of 10% (by g.l.c.). The oxidation of the trithiocarbonate (**13**) was the only case studied in which it was not possible to separate the oxo product from the

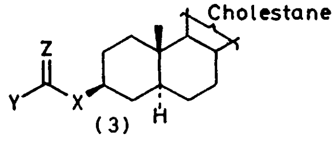


(1)



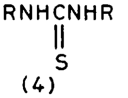
(2)

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



(3)

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

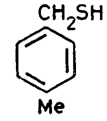


$\mathrm{RNH}\underset{\mathrm{S}}{\underset{\|}{\mathrm{C}}}\mathrm{NHR}$

(4)

a; R = H
b; R = Ph

(5)



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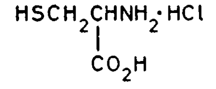
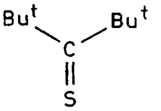


$\mathrm{HSCH_2}\underset{\mathrm{CO_2H}}{\underset{|}{\mathrm{CH}}}\mathrm{NH_2{\cdot}HCl}$

(7)



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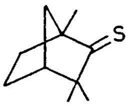
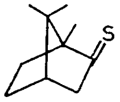
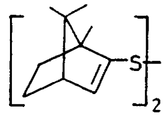


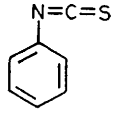
(9)



(10)



(11)



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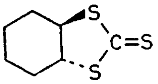
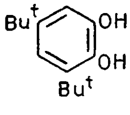


(13)



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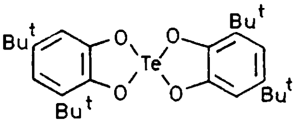

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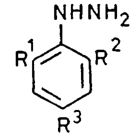

(16)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^2 = H$, $R^3 = Me$
c; $R^1 = R^2 = Me$, $R^3 = H$
d; $R^1 = R^2 = H$, $R^3 = CO_2H$

telluride although sulphur was again isolated in quantitative yield. The catechol (**14**) could be transformed into the *o*-quinone in a yield of 80% while 1,4-dihydroxynaphthalene and quinol were rapidly converted into 1,4-naphthoquinone (97%) and benzoquinone (65%). Tellurium dioxide reacted with (**14**) to produce what appeared to be (**15**) while extended reaction (96 h at room temperature) with 1,4-dihydroxynapthalene gave only a 38% yield of the quinone. Although tellurium dioxide slowly converted thiols into disulphides, it generally did not act as an alternative oxidising agent.

TABLE 2. Oxidation of arylhydrazines.[a]

Compound	Reaction time/h	Yield of hydrocarbon or benzoic acid/%	Yield of telluride R^1TeR^2/% ($R^1 = R^2$ = Anisyl)	($R^1 \neq R^2$)
(**16a**)	0·20	53[b]	68	29
(**16b**)	0·20	30[b]	59	26
(**16c**)	0·20	70[b]	74	5
(**16d**)	24	26[c]	44	d

[a] Reactions carried out at room temperature in dichloromethane with 1·1 equiv. of telluroxide. [b] Yield determined by g.l.c. [c] After aqueous work-up and sublimation. [d] No mixed telluride detected using work-up procedure.

Simple rate studies with (**1**) have shown that (**14**) was oxidised twice as fast as (**2a**) whereas the thiol (**5**) could be selectively oxidised in the presence of (**14**).

The telluroxide (**1**) has also been used for the oxidation of certain nitrogenous compounds (Table 2). Oxidation of the arylhydrazines (**16a–d**) produced the corresponding aromatic hydrocarbon, nitrogen and two tellurium-containing products, the usual bis(*p*-methoxyphenyl) telluride and an unsymmetrical telluride resulting from aryl exchange. 4-Nitro- and 2,4-dinitro-phenylhydrazines gave complex reaction mixtures. Phenylhydroxylamine was readily oxidised by (**1**) to nitrosobenzene in 90% yield.

Of significance is the fact that (**1**) did not react with a number of other fairly easily oxidised substrates such as simple phenols, alcohols, enamines, amines (including pyrrole, indole, tryptophan, tyrosine, aniline, and *NN*-dimethylaniline), oximes, dithiolanes, isonitriles, and 2,4-dinitrophenylhydrazones. Bis(*p*-methoxyphenyl) telluroxide therefore nicely complements other mild and selective oxidising agents that we[2] and others[3] have recently developed.

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[1] G. T. Morgan and R. E. Kellett, *J. Chem. Soc.*, 1926, 1080; J. Bergman, *Tetrahedron*, 1972, **28**, 3323; K. Lederer, *Ber.*, 1916, **49**, 1076.

[2] D. H. R. Barton, A. G. Brewster, R. A. H. F. Hui, D. J. Lester, S. V. Ley, and T. G. Back, *J.C.S. Chem. Comm.*, 1978, 952 and references therein; D. H. R. Barton, J. P. Kitchin, and W. B. Motherwell, *ibid.*, p. 1099.

[3] N. Mikalojczyk and J. Łuczak, *J. Org. Chem.*, 1978, **43**, 2132; S. Tamagaki, I. Hatanaka, and S. Kozuka, *Bull. Chem. Soc. Japan*, 1977, **50**, 3421.