Preparation of Telluro-amides and -hydrazides

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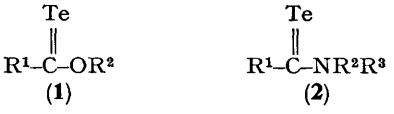
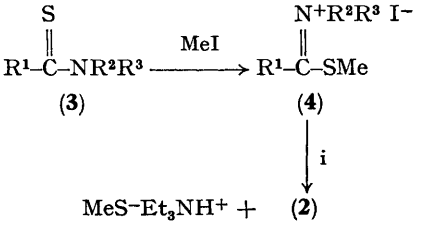
Summary Some peralkylated telluro-amides and -hydrazides were prepared from their thio-analogues by *S*-methylation followed by treatment with hydrogen telluride, and were found to be thermally stable compounds at room temperature.

RECENTLY, Barton *et al.*[1] published the first well documented report on a class of compounds containing the tellurocarbonyl group, *i.e. O*-alkyl tellurocarboxylates (**1**). We report here the preparation and characterization of telluro-amides and -hydrazides (**2**), another class of tellurocarbonyl compounds.



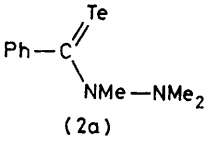
Compounds (**2**) were prepared from the corresponding thio-amides or -hydrazides (**3**) by a route similar to the Shine–Klayman preparation of selenoamides,[2,3] *i.e. S*-methylation of (**3**) followed by treatment of their salts (**4**) with hydrogen chalcogenide ion. However, unlike the selenoamides which are usually formed very smoothly in aqueous ethanol, compounds (**2**) require rather more rigorous conditions for their preparation. Thus the conditions indicated in the Scheme, *i.e.* an aprotic solvent, an inert atmosphere, and a lowered reaction temperature were found to be essential for the successful formation of (**2**).



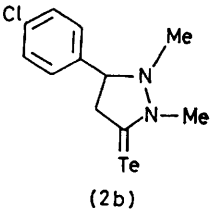
SCHEME. Reagents: i, Et_3N–H_2Te, CH_2Cl_2, Ar, < -40 °C.

In a typical procedure all solvents were purified by passage through alumina and purged with argon prior to use. A solution of the iodide (**4**; R^1 = Ph, R^2 = R^3 = Me) (5 mmol) and triethylamine (5 mmol) in dichloromethane (50 ml) was cooled below −40 °C and dry hydrogen telluride (from 3·5 g of Al_2Te_3) was introduced in a stream of argon. The mixture was left for 1 h and then evaporated *in vacuo*.

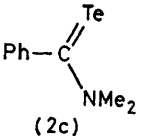
The residue was extracted with toluene. Subsequent slow addition of hexane, at −78 °C, to the filtered toluene extract yielded the tellurobenzohydrazide (**2a**) as brick-red crystals.



(2a)



(2b)



(2c)

TABLE. Data for the telluro-amides and -hydrazides (**2**).[a]

Compound	Yield/ %	M.p. (*t*/°C)	U.v.–vis. λ_{max}/nm(log ϵ)	^{1}H N.m.r. δ(CTe–NMe)
(**2a**)	19	100	375 (4·00)[b]	3·62
			540 (3·02)	
(**2b**)	5	120	370 (4·10)	3·60
			465 (3·27)	
(**2c**)	15	73	387 (3·99)	3·75
			540 (2·91)	2·98

[a] Compounds (**2**) gave satisfactory elemental analyses (C, H, and N) and correct molecular ions (^{130}Te) in the mass spectrum. U.v.–visible and ^{1}H n.m.r. spectra were recorded in CCl_4. All m.p.s. are with decomposition. [b] For comparison the u.v.–visible data for the seleno-analogue of (**2a**) are λ_{max} (log ϵ) 316 (4.09) and 442 nm (2.6).

Data for compounds (**2a**—**c**) prepared in this way are given in the Table. The structure assignment is based upon the following spectroscopic observations. (i) The i.r. spectra (4000—300 cm^{-1}) of (**2**) are almost superimposable on those of the respective seleno-analogues with no band displacement exceeding *ca.* 20 cm^{-1}. The same pattern is observed when seleno- and thio-amides are compared.[4] (ii) The u.v.–visible spectra of (**2**) compared with those of the seleno-analogues show red shifts of both the $\pi \rightarrow \pi^*$ and the $n \rightarrow \pi^*$ absorption as well as an enhanced extinction coefficient of the latter (Table). (iii) The ^{1}H n.m.r. spectra of (**2**) all show a strongly deshielded amidic N–Me group (δ 3·6—3·75).

Compounds (**2**) are stable at room temperature in the absence of moisture, although (**2c**) had decomposed slightly after 1 h in refluxing toluene. However, they are rapidly attacked by the atmosphere or by wet solvents to give the corresponding amides and elemental tellurium. This degradation is catalysed by common chromatographic materials such as alumina and silica gel and it has thus not been possible to apply chromatography to the isolation of (**2**). The process appears to be a rapid hydrolysis followed by oxidation of the liberated hydrogen telluride and indicates that the instability of tellurocarbonyl compounds is derived mainly from a strong electrophilic reactivity. In fact, we believe that stabilization by adjacent donor groups in (**2**) is a major reason for the successful isolation of these compounds implying that another way of stabilizing tellurocarbonyl compounds would be the introduction of bulky groups which would screen the tellurocarbonyl function against nucleophilic attack. Such screening may well be contributing to the remarkable stability of the tellurocarboxylic esters (**1**) described by Barton.[1]

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[1] A. G. M. Barret, D. H. R. Barton, and R. W. Read, *J.C.S. Chem. Comm.*, 1979, 645.
[2] D. L. Klayman and R. J. Shine, *Chem. Comm.*, 1968, 372.
[3] D. L. Klayman and R. J. Shine, *J. Org. Chem.*, 1968, **34**, 3549.
[4] K. A. Jensen, L. Henriksen, and P. H. Nielsen, in 'Organic Selenium Compounds,' eds. D. L. Klayman and W. H. H. Günther, Wiley, New York, 1973, p. 849.