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Chemoselective Reactions of Tellurium Tetraethoxide towards Thioamides and Amides

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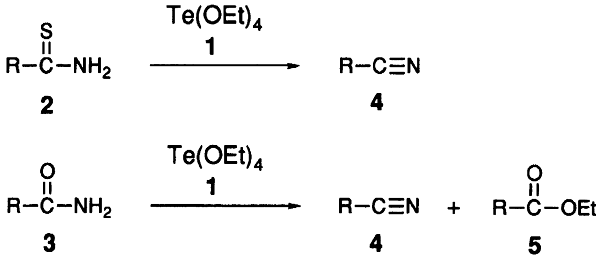
Synopsis. Tellurium tetraethoxide reacts with primary thioamides at room temperature, forming nitriles in high yields. On the other hand, the reactions with amides are largely temperature-dependent, giving predominantly esters at 80 °C and nitriles at a higher temperature. Similarly, tellurium tetraethoxide readily induces the C–N bond cleavage of ureas to give carbamates and amines.

Much attention has recently been focused on the development of novel organotellurium compounds that are useful for organic syntheses.[1)] Although tellurium tetraalkoxides have been known for a long time, nothing has been studied with respect to their reactivities, except for the replacement of the alkoxyl groups by other ligand groups.[2)] Such tetracoordinated tellurium compounds have great potential as versatile reagents, due to their hypervalent nature, as represented by the reactions of tellurium tetrachloride.[3)] In this paper we describe that readily available tellurium tetraethoxide (**1**)[4)] can induce chemoselective reactions towards thioamides (**2**) and amides (**3**) involving ureas to form nitriles (**4**) or esters (**5**) (Scheme 1).

Results and Discussion

The reactions of tellurium tetraethoxide (**1**) with primary thioamides (**2**) smoothly proceeded in chloroform at room temperature to give the corresponding nitriles (**4**) in high yields: R=Ph, 96%; R=4-ClC_6H_4, 79%; R=4-$O_2NC_6H_4$, 86%; R=4-MeC_6H_4, 70%; R=4-$MeOC_6H_4$, 90%; R=3-pyridyl, 76%; R=$PhCH_2$, 74%; R=$CH_3(CH_2)_{16}$, 87%; R=Ph_2N, 98%.

In contrast to the thioamides, the reactions of primary amides (**3**) with **1** in carbon tetrachloride under reflux led to a mixture of nitriles (**4**) and esters (**5**). As shown in Table 1, the esters are generally the major products, with the product ratios being fairly dependent on the substrate structure. In general, the introduction of an electron-donating group into the phenyl ring of benzamide tends to favor the formation of nitrile, whereas that of an electron-withdrawing group does promote the formation of ester. Nicotinamide and cinnamamide favored the formation of the esters (Runs 11 and 12). In addition, alkanamides, such as 2-phenylacetamide, 3-phenylpropionamide, and dodecanamide, reacted more quickly to give the corresponding esters almost exclusively (Runs 13—15). More interestingly, the product ratios are greatly temperature-dependent, as shown in detail in the reaction of *p*-chlorobenzamide (Runs 2—7). The formation of the ester **5** was favored at 80 °C, while an increase in the temperature not only made the reaction time shorter, but also prompted the formation of the nitrile **4**; the selectivity was reversed in refluxing 1,2-dichloroethane or toluene, and the highest selectivity of the nitrile **4** was marked in refluxing 1,1,2,2-tetrachloroethane.



Scheme 1.

Although tellurium tetraethoxide (**1**) was also reactive towards *N*-substituted amides, the yields were very low; the reaction with *N*-phenylbenzamide in refluxing carbon tetrachloride for 25 h gave a mixture of ethyl benzoate (36%) and aniline (16%) and that with *N*-methylnicotinamide gave ethyl nicotinate in only 5% yield. On the other hand, no reaction occurred with *N*,*N*-disubstituted amides, such as *N*,*N*-dimethylbenzamide, *N*,*N*-diethyl-3-phenylpropionamide and *N*,*N*-diphenyl-3-phenylpropionamide.

Tellurium tetraethoxide (**1**) readily effected the ethanolysis of ureas. As shown in Table 2, carbamates and amines are produced by the cleavage of either of the two C–N bonds. For example, the reactions of *N*,*N*-diphenylurea and 5*H*-dibenz[*b*,*f*]azepine-5-carboxamide in refluxing carbon tetrachloride for 3 h cleaved the substituted amide bond to afford the corresponding amine as a sole isolated product in high yields. On the other hand, the reactions of phenylurea and benzylurea mainly cleaved the nonsubstituted amide bond to yield carbamates. The reaction of benzoylurea gave a mixture of three products; benzamide and ethyl benzoate were produced by the cleavage of the two substituted amide bonds, whereas benzonitrile was formed by a subsequent dehydration of the resulting benzamide. The ethanolysis of *N*,*N'*-diphenylurea occurred at reflux in 1,1,2-trichloroethane to give aniline and ethyl *N*-phenylcarbamate in low yields.

A plausible mechanism for the chemoselective reactions of tellurium tetraethoxide (**1**) with thioamides (**2**) and amides (**3**) is shown in Scheme 2.[5)] In the reaction with thioamide, **1** initially bonds to the sulfur atom in exchange for an ethoxy ligand to give intermediate

Table 1. Reactions of Various Primary Amides (**3**) with Tellurium Tetraethoxide (**1**)[a]

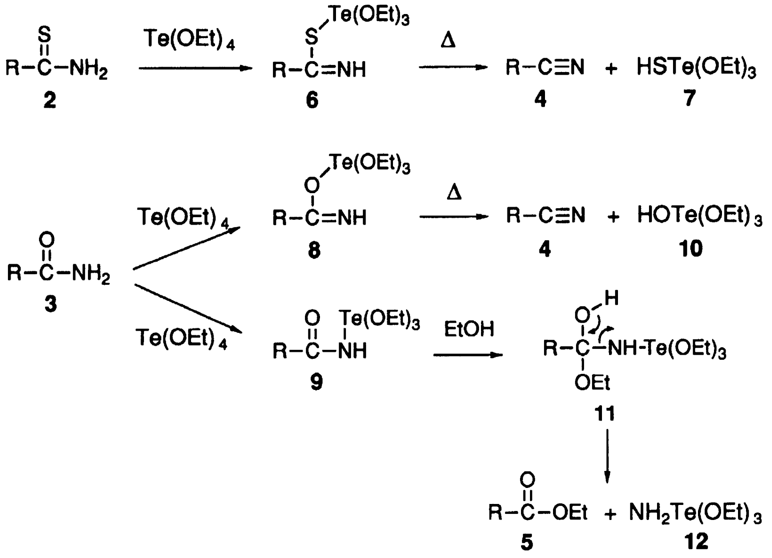
Run	R in **3**	Solvent	Temp	Time h	Yield/% Nitrile (**4**)	Yield/% Ester (**5**)
1	Ph	CCl_4	Reflux	18	28	52
2	4-ClC_6H_4	CCl_4	Reflux (77 °C)	18	15	77
3		Benzene	Reflux (80 °C)	18	27	56
4		$ClCH_2CH_2Cl$	80 °C	18	19	42
5		$ClCH_2CH_2Cl$	Reflux (113 °C)	5	61	22
6		Toluene	Reflux (111 °C)	4	43	27
7		$Cl_2CHCHCl_2$	Reflux (147 °C)	2	58	13
8	4-$O_2NC_6H_4$	CCl_4	Reflux	18	6	91
9	4-MeC_6H_4	CCl_4	Reflux	18	35	57
10	4-$MeOC_6H_4$	CCl_4	Reflux	18	36	35
11	3-Pyridyl	CCl_4	Reflux	18	8	79
12	*trans*-PhCH=CH	CCl_4	Reflux	10	15	67
13	$PhCH_2$	CCl_4	Reflux	3	0	62
14	$PhCH_2CH_2$	CCl_4	Reflux	3	7	84
15	$CH_3(CH_2)_{10}$	CCl_4	Reflux	5	0	74

a) An equimolar amount of **1** was used. b) Isolated yields.

Table 2. Reactions of Ureas with Tellurium Tetraethoxide (**1**)[a]

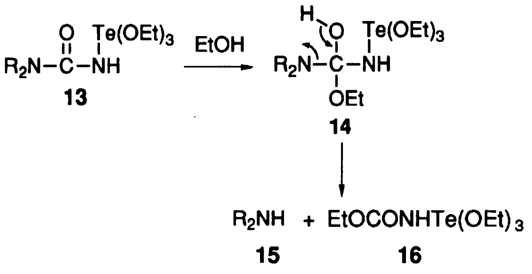
Run	Urea	Product (Yield/%)[b]
1	Ph_2NCONH_2	Ph_2NH (81)
2	5*H*-Dibenz[*b*,*f*]azepine-5-carboxamide	5*H*-Dibenz[*b*,*f*]azepine (85)
3	$PhNHCONH_2$	$PhNHCO_2Et$ (80), $PhNH_2$ (7)
4	$PhCH_2NHCONH_2$	$PhCH_2NHCO_2Et$ (33)
5	$PhCONHCONH_2$	$PhCONH_2$ (39), $PhCO_2Et$ (21), PhCN (4)
6	PhNHCONHPh[c]	$PhNH_2$ (35), $PhNHCO_2Et$ (15)

a) The reactions were carried out in refluxing carbon tetrachloride for 3 h unless otherwise stated. b) Isolated yields. c) Conditions: refluxing for 17 h in 1,1,2-trichloroethane.



Scheme 2.

(**6**), which undergoes degradation to form nitrile (**4**). This dehydrosulfurization process might be ascribed to a strong tellurium-sulfur affinity. In the case of amide (**3**), either of the oxygen and nitrogen atoms can coordinate to the tellurium to form an oxygen-ligated intermediate (**8**) or a nitrogen-ligated one (**9**). The degradation reaction of **8** to nitrile (**4**) requires a higher temperature than that of **6** because of the strong C–O bond. Thus, the ethanolysis of **9** precedes the dehydration process, giving the ester (**5**) together with the tellur-


Scheme 3.

amide (**12**). This ethanolysis probably proceeds via the adduct (**11**), and accordingly, is suppressed by accelerating the pyrolytic dehydration process at a higher temperature. The sluggish ethanolysis of *N*-substituted amides may be attributed to sterical hindrance. Needless to say, the inertness of *N*,*N*-disubstituted amides is due to an impossible ligand exchange. The higher reactivity of ureas than that of amides reflects ready C–N bond breaking due to less conjugation. The exclusive formation of the amines from *N*,*N*-diphenylurea and 5*H*-dibenz[*b*,*f*]azepine-5-carboxamide can be explained by a path via a common intermediate (**13**) ligated at the nonsubstituted nitrogen atom (Scheme 3). Cleavage of the substituted amide bond, rather than the nonsubstituted amide bond in **14**, is ascribed to the high basicity of the disubstituted nitrogen atom.

In summary, tellurium tetraethoxide (**1**) induces a novel dehydrosulfurization of the thioamides and dehydration or ethanolysis of amides. Since the alcoholyses or hydrolyses of amides generally require severe conditions, the present method with **1** is of particular interest.

Experimental

Preparation of Tellurium Tetraethoxide. To a sodium ethoxide solution, prepared from sodium (3.22 g, 140 mmol) and absolute ethanol (100 ml), was slowly added an ice-cooled solution of tellurium tetrachloride (9.43 g, 35 mmol) in 1 : 1 tetrahydrofuran–benzene (100 ml) under an argon atmosphere. The mixture was stirred for 1.5 h at room temperature, and the solvent was evaporated under argon. The residue was distilled in vacuo to give a colorless oil of tellurium tetraethoxide, 7.22 g (67%), bp 106 °C/5 Pa (lit,[4] bp 100 °C/0.25 Pa). Because of the relative sensitivity to moisture and fumes in air, it was stocked as 20% wt solution in carbon tetrachloride under argon in a sealed tube equipped with a septum cap.

General Procedure for the Reactions of Thioamides and Amides with Tellurium Tetraethoxide. To a solution of 4-nitrothiobenzamide (218.6 mg, 1.20 mmol) in dry chloroform (20 ml) was added a solution of tellurium tetraethoxide (385 mg, 1.25 mmol) in carbon tetrachloride in an argon atmosphere. The mixture was stirred for 1 h at room temperature, washed with 3% aq sodium hydrogencarbonate and then extracted with chloroform. The extract was filtered through celite to remove a black tellurium precipitate which was formed. The filtrate was evaporated in vacuo, and the residue was purified by column chromatography on silica gel using chloroform as an eluent, followed by recrystallization from ethanol to give colorless leaflets of 4-nitrobenzonitrile (152 mg, 86%); mp 149.5—150.5 °C (lit,[6] mp 147.5—148.5 °C); ^{1}H NMR (60 MHz, $CDCl_3$) δ=7.92 (d, J=8.9 Hz, 2H), 8.37 (d, J=8.9 Hz, 2H); IR (KBr disk) 3100, 2330, 1605, 1525, 1350, 860, 750 cm^{-1}; MS (70 eV) m/z 148 (M^+).

The reactions of other thioamides and amides were carried out in a similar manner, and the mixtures of the nitriles **4** and the esters **5** were separated by gel-permeation liquid chromatography using chloroform as an eluent. All of the products were characterized by a comparison of their melting points (except the oily products) and spectral data[7] with those of the commercially available authentic samples.

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