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Benzenetellurinic Mixed Anhydrides as Mild Oxidizing Agents[1)]

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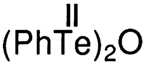
Three benzenetellurinic mixed anhydrides, i.e., benzenetellurinyl acetate, trifluoroacetate, and trifluoromethanesulfonate, have been found to be mild oxidizing agents for various substrates such as thiol, phosphine, acyloin, α-hydroxy ester, catechol, hydroquinone, thiourea, and thioamide. The reactions towards the last two substrates are highly chemoselective, depending on both the reagent and substrate.

Arenetellurinic anhydride,[2)] like telluroxide,[3)] and tellurone,[4)] behaves as a mild oxidizing agent based on its weak Te=O bond. However, it has the disadvantage of being insoluble in common solvents except acetic acid. We recently found that ready solubilization of benzenetellurinic anhydride (**1**) in acetic acid was caused by its conversion to benzenetellurinyl acetate (**2**).[5)] The same conversion occurred with equimolar acetic anhydride in an appropriate solvent. In addition, treatment with trifluoroacetic anhydride or trifluoromethanesulfonic anhydride gave the corresponding mixed anhydrides **3** and **4**, respectively. These mixed anhydrides turned out to act as superior electrophiles, inducing novel cyclofunctionalization of functionalized olefins.[5)] One might wonder whether the mixed anhydrides are sensitive to some functional groups as does tellurinic anhydride (**1**). This has prompted us to examine their reactivities towards various substrates in detail. We now report the mild oxidative properties of **2**-**4**, which are found to be somewhat different from one another.


$(\mathrm{Ph}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Te}})_2\mathrm{O}$

1


$\mathrm{Ph}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Te}}\mathrm{OCOCH_3}$

2


$\mathrm{Ph}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Te}}\mathrm{OCOCF_3}$

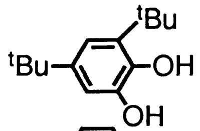
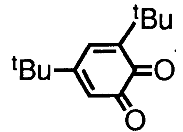
3


$\mathrm{Ph}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{Te}}\mathrm{OSO_2CF_3}$

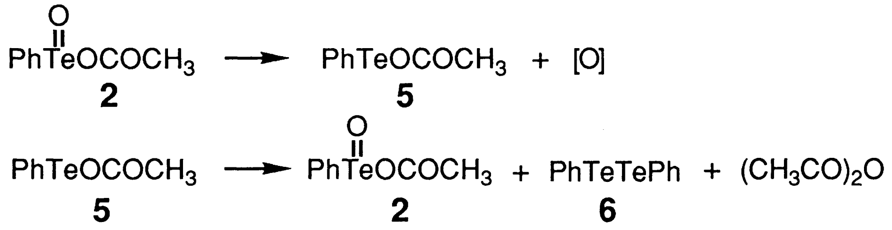
4

The mixed anhydrides **2**-**4** were inert to simple alcohol, benzylic alcohol, phenol, ketone and amine, but reactive to thiol, phosphine, acyloin, α-hydroxy ester, catechol, and hydroquinone as summarized in Table 1.[6)] Any reagent could

Table 1. Oxidative Reactions with Benzenetellurinic Mixed Anhydrides **2**-**4**

Run	Substrate	Solvent	Temp	Time/h	Product	Isolated yield/%		
						2	**3**	**4**
1	PhSH	CH_2Cl_2	RT	0.5	PhSSPh	90	93	95
2	Ph_3P	CH_2Cl_2	RT	1	Ph_3PO	93	94	95
3	PhCH(OH)COPh	CH_2Cl_2	RT	1.5	PhCOCOPh	50	99	26
4	^{n}BuCH(OH)CO^{n}Bu	$CHCl_3$	Reflux	1.5	^{n}BuCOCO^{n}Bu	88	100	43
5	$PhCH(OH)CO_2Me$	PhH	Reflux	12	$PhCOCO_2Me$	59	76	trace
6		$CHCl_3$	Reflux	12		40	18	trace
7		$CHCl_3$	Reflux	24		38	28	0

smoothly oxidize thiophenol to diphenyl disulfide and triphenylphosphine to the phosphine oxide at room temperature. The exact stoichiometry of the reagent was 1/3 mole per thiophenol and 2/3 mole per triphenylphosphine, and the reagent was reduced almost quantitatively to diphenyl ditelluride (**6**). Therefore, a plausible mechanism for the degradation of **2** is proposed in Scheme 1, which proceeds via reduction to benzenetellurenyl acetate (**5**) followed by disproportionation to **2** and **6**.

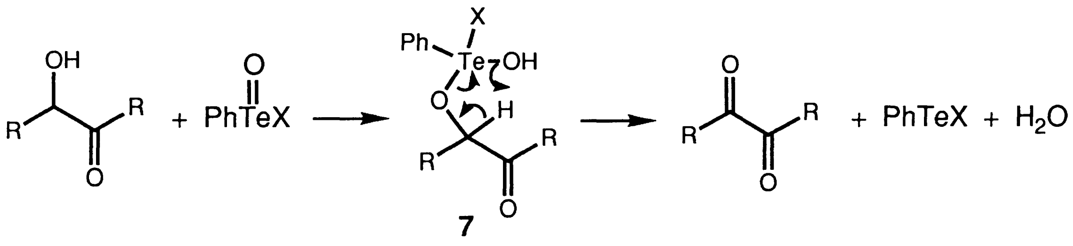


$$\underset{\mathbf{2}}{\mathrm{Ph\overset{O}{\overset{\|}{Te}}OCOCH_3}} \longrightarrow \underset{\mathbf{5}}{\mathrm{PhTeOCOCH_3}} + [\mathrm{O}]$$

$$\underset{\mathbf{5}}{\mathrm{3\,PhTeOCOCH_3}} \longrightarrow \underset{\mathbf{2}}{\mathrm{Ph\overset{O}{\overset{\|}{Te}}OCOCH_3}} + \underset{\mathbf{6}}{\mathrm{PhTePh}} + \mathrm{(CH_3CO)_2O}$$

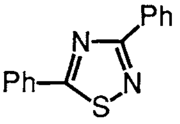
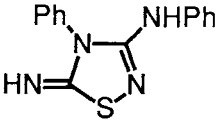
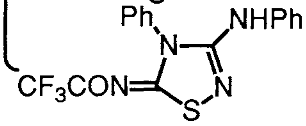
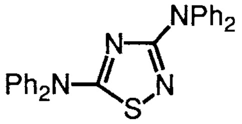
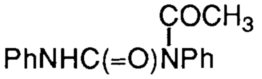
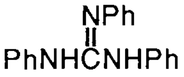
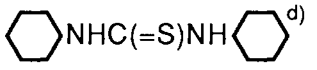
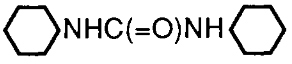
Scheme 1.

The oxidation of hydroxy substrates with the mixed anhydrides largely depends on both of the substrate and the reagent. Thus, reagent **3** readily oxidized benzoin to benzil at room temperature, valeroin to 5,6-decanedione in refluxing chloroform, and methyl mandelate to methyl phenylglyoxylate in refluxing benzene. It also reacted with catechol and hydroquinone, though the conversion efficiency to



Scheme 2.

Table 2. Selective Reactions Depending on Mixed Anhydrides **2**-**4**

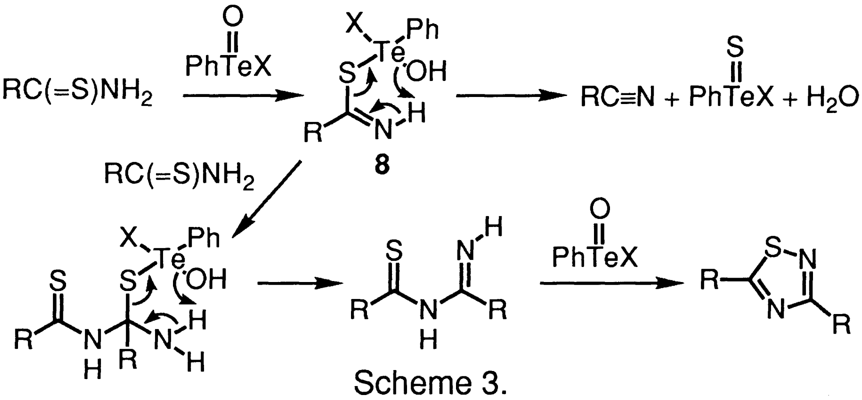
Run	Substrate	Product	Yield/%		
			2	**3**	**4**
1	$PhC(=S)NH_2$[a)]	$PhC{\equiv}N$	80	68	trace
			0	20	71
2	$PhNHC(=S)NH_2$[b)]	$PhNHC{\equiv}N$	79	0	0
			0	56	96
			----	26	----
3	$Ph_2NC(=S)NH_2$[b)]	$Ph_2NC{\equiv}N$	91	14	5
			trace	68	59
4	$PhNHC(=S)NHPh$[c)]	$PhNHC(=O)NHPh$	32	58	0
		 $PhNHC(=O)N(COCH_3)Ph$	66	----	----
		 $PhNHC(=NPh)NHPh$	0	30	10
5			77	82	27

Conditions: a) CH_2Cl_2, RT, 0.5 h, b) $CHCl_3$, 50 °C, 3 h,
c) $CHCl_3$, RT, 12 h, d) CH_2Cl_2, RT, 12 h.

quinones was very low. On the other hand, **2** was less reactive towards the former substrates but more reactive towards the latter substrates. Furthermore, **4** was quite inactive to all the substrates. The oxidations of the hydroxy compounds presumably proceed via tellurium(IV) adduct **7** (Scheme 2). Since such hypervalent species are stabilized by electron withdrawing ligands, the slow reactions with reagent **4** are ascribable to high stabilization of its adduct **7**.

The mixed anhydrides **2**-**4** effected the reactions of thioamides and thioureas, which were highly chemoselective. As shown in Table 2, reagent **2** effected predominant elimination reaction of thiobenzamide, phenylthiourea, and *N*,*N*-diphenylthiourea to the corresponding nitriles, whereas reagent **4** favored oxidative dimerization reaction to 1,2,4-thiadiazole derivatives. Reagent **3** exercised double-faced selection, i.e., thiobenzamide to benzonitrile and thiourea to the thiadiazole.

These chemoselective reactions are reminiscent of those with diaryl tellurium(IV) species.[7] Scheme 3 shows a reasonable mechanism for transformations into the two products. The selectivity again depends on facility in decomposition of hypervalent adduct **8**. Thus the ready elimination directly leads to nitrile, otherwise dimerization occurs, finally leading to 1,2,4-thiadiazole. Furthermore, Table 2 shows that the mixed anhydrides **2** and **3** could convert symmetrical *N,N'*-diphenylthiourea and *N,N'*-dicyclohexylthiourea into the corresponding urea derivatives as the main products. In contrast, the reactions with **4** hardly gave such products. These different reactivities also seem to be related to degradation of the hypervalent tellurium adducts.



Scheme 3.

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6) All reaction products in the present paper were isolated and characterized by spectroscopic and elemental analyses.
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