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NOVEL OXIDIZING PROPERTIES OF p-METHOXYBENZENETELLURINIC ACID ANHYDRIDE1)

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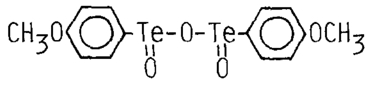
Abstract: The title compound has proved to be a mild oxidizing agent like the corresponding telluroxide or tellurone towards thiol, phosphine, thioamide, thiourea, thionoester, and benzylic alcohol. In addition, it serves as a selective catalyst for the hydration of terminal alkyne.

Although organotellurinic acid anhydrides have been known since many years ago, their chemical properties have been little investigated.2) They are expected to have a potential oxidizing ability like organotelluroxide3) and tellurone4) due to their similar labile Te-O bonds. Very recently Barton et al. reported that aryltellurinic acid anhydrides were mild oxidizing agents towards thiols, hydroquinones, and xanthates.5) In addition, Sonoda et al. presented that benzenetellurinic acid anhydride induced acetoxylation of olefins and ketones with acetic acid.6) These reports prompt us to report our independent study on the reactivity of p-methoxybenzenetellurinic acid anhydride 1, which is similar in many respects to that of the corresponding diaryl telluroxide **2** or tellurone **3**.



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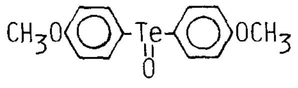

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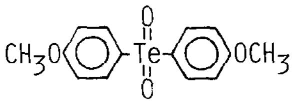

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p-Methoxybenzenetellurinic acid anhydride **1** is readily accessible by treatment of anisole with tellurium tetrachloride,7) followed by alkaline hydrolysis of the resulting p-methoxyphenyltellurium trichloride.2) It is insoluble in usual solvents except acetic acid, but as an oxidation with it proceeds, it is reduced to readily soluble bis(p-methoxyphenyl)ditelluride. As shown in Table 1, **1** like telluroxide **2**3,8) smoothly reacted with thiol, phosphine, thioamide, and thionoester to give disulfide, phosphine oxide, nitrile, and ester, respectively (Runs 1-6), though the last reaction required somewhat severe conditions. In addition, **1** effected the conversion of N,N'-diphenylthiourea into N,N'-diphenylcarbodiimide (Run 7), in contrast to the reaction with telluroxide **2** leading to N,N'-diphenylurea. Diaryltelluroxide **2** does not react with simple alcohols, but diaryltellurone **3** is capable of oxidizing benzylic alcohols to the corresponding carbonyl compounds.4) Such transformations could also be carried out using **1** (Runs 8-11).

Table 1. Oxidative reactions with p-methoxybenzenetellurinic acid anhydride 1

Run	Substrate	Solvent	Temp	Time/h	Product	Yield/%
1	p-$H_2NC_6H_4SH$	CH_2Cl_2	RT	0.16	(p-$H_2NC_6H_4S)_2$	95
2	Ph_3P	CH_2Cl_2	RT	24	Ph_3PO	92
3	$PhCSNH_2$	CH_2Cl_2	RT	0.5	PhCN	95
4	p-$ClC_6H_4CSNH_2$	CH_2Cl_2	RT	0.5	p-ClC_6H_4CN	91
5	Ph_2NCSNH_2	AcOH	RT	24	Ph_2NCN	63
6	$PhCSOCH_3$	$CHCl_3$	Reflux	24	$PhCOOCH_3$	60
7	PhNHCSNHPh	CH_2Cl_2	RT	1	PhN=C=NPh	89
8	p-$O_2NC_6H_4CH_2OH$	Toluene	Reflux	24	p-$O_2NC_6H_4CHO$	94
9	p-$CH_3OC_6H_4CH_2OH$	Xylene	Reflux	22	p-$CH_3OC_6H_4CHO$	91
10	PhCH(OH)COPh	Toluene	Reflux	0.16	PhCOCOPh	95
11	$CH_3CH(OH)COOCH_3$	Neat	130°C	1	$CH_3COCOOCH_3$	90

Another useful reaction of 1 has been discovered towards alkynes. Tellurinic acid anhydride 1 was usually inert to non-terminal alkynes except for the conversion of diphenylacetylene into benzil with the aid of sulfuric acid. On the other hand, 1 catalyzed the hydration of terminal alkynes in acetic acid at reflux. Some results are shown in Table 2. It should be noted that 1,6-undecadiyne suffered the selective hydration of only the terminal acetylene (Run 4). Thus, the present method nicely complements the conventional hydration method using a mercuric catalyst which is applicable to both terminal and non-terminal acetylenes.

A reasonable mechanism for the hydration of terminal alkyne with 1 is proposed as below.

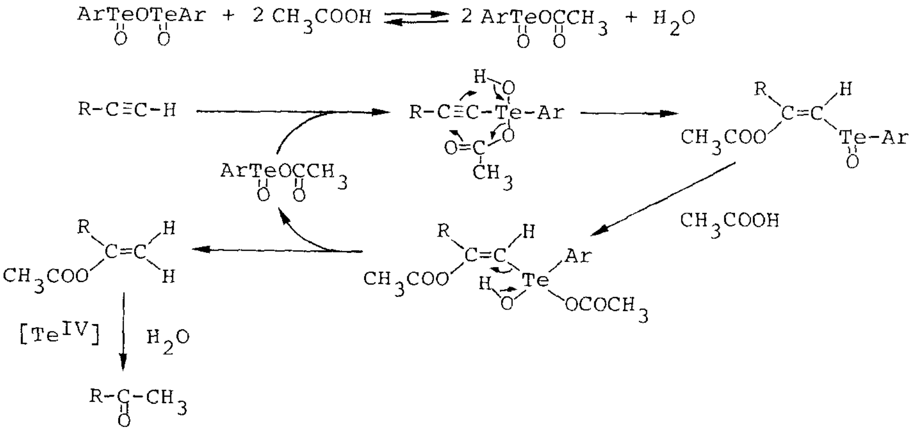
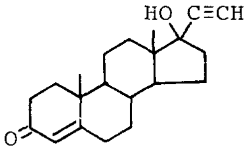
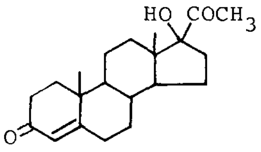
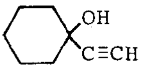
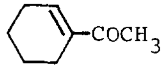
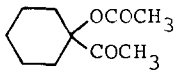


Table 2. Reactions of alkynes with 10 mol% of p-methoxybenzenetellurinic acid anhydride 1 in acetic acid at reflux[a]

Run	Substrate	Product	Yield/%
1	$PhC{\equiv}CH$	$PhCOCH_3$	89
2	$n\text{-}C_6H_{13}C{\equiv}CH$	$n\text{-}C_6H_{13}COCH_3$	90
3	$HC{\equiv}C(CH_2)_6C{\equiv}CH$	$CH_3CO(CH_2)_6COCH_3$	91
4	$n\text{-}C_4H_9C{\equiv}C(CH_2)_3C{\equiv}CH$	$n\text{-}C_4H_9C{\equiv}C(CH_2)_3COCH_3$	85
5			93
6			58
			32
7	$n\text{-}C_6H_{13}C{\equiv}CCH_3$	No reaction	
8	$PhC{\equiv}CCH_3$	No reaction	
9	$PhC{\equiv}CPh$	No reaction	
10	$PhC{\equiv}CPh$[b]	PhCOCOPh	61

a) Reaction time 20 h.

b) Equimolar amount of 1 and catalytic amount of sulfuric acid were used.

Typical experimental procedures using p-methoxybenzenetellurinic acid anhydride 1 are exemplified as follows.

A general procedure of oxidation: Thiobenzamide (0.15 g, 1.09 mmol) was mixed with p-methoxybenzenetellurinic acid anhydride 1 (0.189 g, 0.356 mmol) in 4 ml of dry dichloromethane. The suspension was stirred at room temperature in a nitrogen atmosphere and became clear in 0.5 h. After the solvent was evaporated under a reduced pressure, benzonitrile was separated from the product mixture by bulb-to-bulb distillation at bp 122-123°C/100 mmHg, yield 0.107 g (95%). Column chromatography of the residue on silica gel using benzene as eluent gave red crystals of bis(p-methoxyphenyl)ditelluride, 0.152 g.

A general procedure of hydration: A mixture of phenylacetylene (0.153 g, 1.5 mmol) and p-methoxybenzenetellurinic acid anhydride 1 (0.08 g, 0.15 mmol) in 4 ml of acetic acid was stirred at reflux for 20 h in a nitrogen atmosphere. After the solvent was evaporated under a reduced pressure, 10 ml of ether was added, and the ethereal solution was washed with 5% aq. sodium bicarbonate, and dried on anhydrous magnesium sulfate. After concentration of the solution, column chromatography of the residue on silica gel using benzene as eluent gave a colorless oil of acetophenone, yield 0.161 g (89%).

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