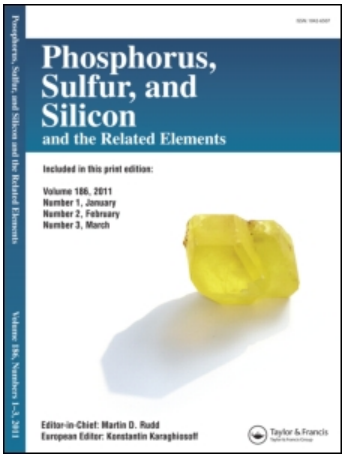


## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# New Synthetic Reactions Using Some Organotelluriums

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**To cite this Article** Ogura, Fumio , Otsubo, Tetsuo and Aso, Yoshio(1992) 'New Synthetic Reactions Using Some Organotelluriums', Phosphorus, Sulfur, and Silicon and the Related Elements, 67: 1, 223 — 238
**To link to this Article: DOI:** 10.1080/10426509208045840
**URL:** http://dx.doi.org/10.1080/10426509208045840

*Phosphorus, Sulfur, and Silicon*, 1992, Vol. 67, pp. 223-238 
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# NEW SYNTHETIC REACTIONS USING SOME ORGANOTELLURIUMS

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Abstract Organotelluriums exhibit versatile reactivities of great interest, which include abundunt potentialities to be utilized for organic synthesis. In this paper some new reactions and syntheses of organotelluriums are discussed.



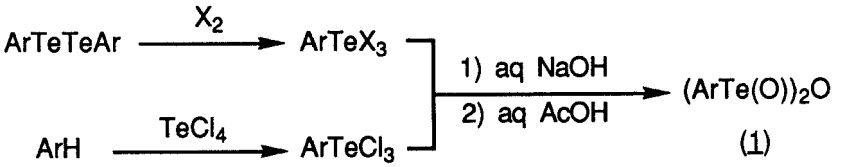
## INTRODUCTION

Tellurium, a typical element sitting on the 5th row of 16th(6B) group, has both metallic and non-metallic nature and shows variable valences. Recently organotellurium chemistry attracts much attention from the viewpoint of development of new synthetic methodology and synthesis of new advanced materials. In this paper new reactions of arenetellurinic anhydrides and diisobutylaluminum benzenetellurorate are described. Both of the reagents were developed in our group. The former is a mild oxidizing agent as well as a soft electrophile and the latter is a complex reagent composed of a soft base and a hard acid. Furthermore, a new reaction of tellurium tetrachloride, a commercially available reagent, with thioamides and related compounds is introduced.

## REACTIONS OF ARENETELLURINIC ANHYDRIDES

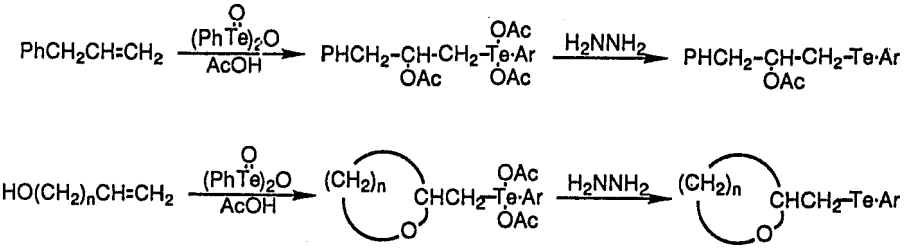
Organotellurinic acids and their anhydrides have been known since many years ago; however, their chemical properties are becoming actively studied only very recently. They are expected to have a potential oxidizing ability like organotelluroxides and tellurones due to their similar labile Te-O bond. And they may behave as soft electrophiles to afford $ArTe(O)^+$ on heterolysis. Arenetellurinic anhydrides are readily accessible by alkaline hydrolysis of arenetellurium trihalides and subsequent acidification. Arenetellurium trihalides are easily obtained by treatment of diaryl ditellurides with halogen ($X_2$) or by reaction of reactive arenes with tellurium tetrachloride as shown

below (a, Ar=Ph; b, Ar=p-$CH_3OC_6H_4$; c, Ar=2-Naphthyl). The anhydrides are insoluble in usual solvents except acetic acid, but as oxidative reactions proceed they dissolve gradually and are recovered as diaryl




ditellurides after workup. Recently we[1] and Barton[2] reported that arenetellurinic anhydrides (1) behave as mild oxidizing agents toward various kind of organic compounds. Thus, thiols, phosphines, thioamides, thioureas, thioesters, acyloins, and benzylic alcohols are easily oxidized to disulfides, phosphine oxides, nitriles, carbodiimides, esters, α-diketones, and benzaldehydes by 1, respectively.[3] Furthermore, 1 catalyzes the hydration of terminal alkynes in AcOH.[3]

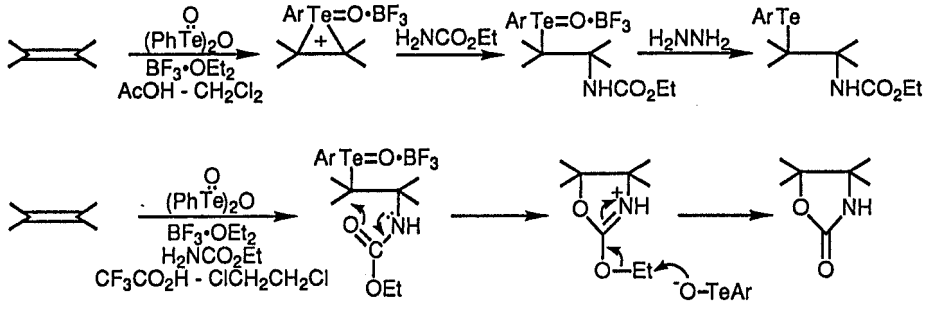
We found that 1 reacts with olefins in AcOH under the catalytic influence of Lewis acid such as $BF_3 \cdot O(C_2H_5)_2$ to afford acetoxytellurinylated products. The reaction shows high Markovnikov regio- and anti stereo-selectivity. It is initiated by an electrophilic addition of arenetellurinyl cation and followed by a nucleophilic attack of the solvent, AcOH. If an effective nucleophilic group OH is present at the suitable position in the olefinic molecule, an intramolecular cyclization, cyclofunctionalization of hydroxy olefins, occurs to afford




Scheme 1.

cyclic ether bearing aryltelluromethyl group (Scheme 1).[4] A similar reaction, aminotellurinylation, of olefins occurs with 1 and alkyl carbamates under the catalysis of Lewis acid in AcOH or $CF_3CO_2H$. Thus, when excess ethyl carbamate and $BF_3 \cdot OEt_2$ are added to a refluxed

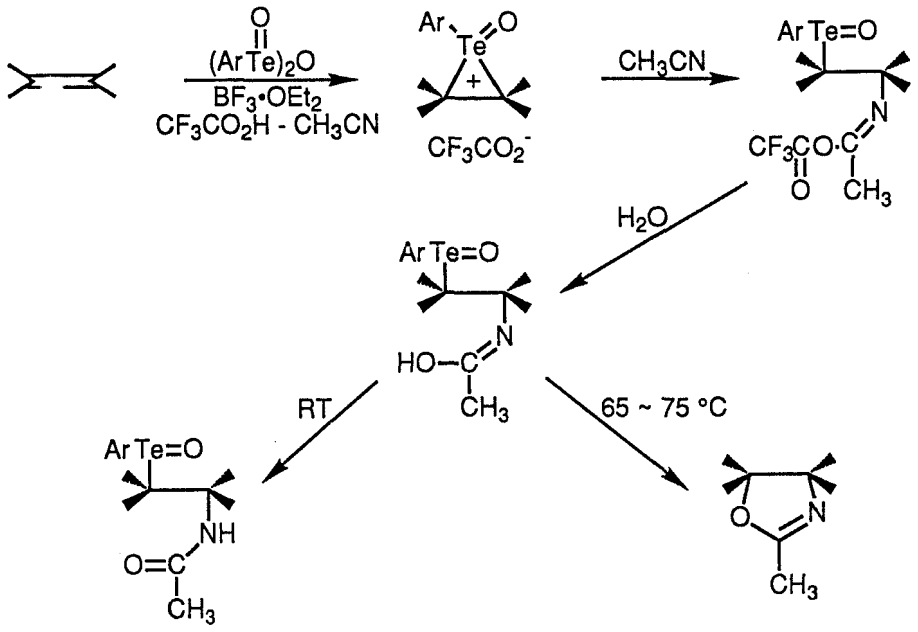
mixture of olefin, 1, AcOH or $CF_3CO_2H$, and $CH_2Cl_2$ or $CHCl_3$, aminotellurinylation occurs in preference to acetoxytellurinylation, giving ethyl β-(aryltelluro)alkyl carbamate obeying high Markovnikov regio- and anti stereo-selectivity. When olefins having a carbamate group at the suitable position are employed, similar cyclofunctionalization as in the case of acetoxytellurination, an intramolecular cyclization occurs to give nitrogen heterocycles bearing aryltelluromethyl group. The reactions are more effective in $CF_3CO_2H$ than $CH_3CO_2H$ to improve the yield.[5] Furthermore, when the reaction is carried out at a higher temperature, for example, in refluxed 1,2-$ClCH_2CH_2Cl$, the oxazolidine-2-one is obtained in high yield instead of the allylic amide to be produced by telluroxide elimination of the aminotellurinylation product. The reaction occurs with high net cis stereoselectivity. So we suggested that the reaction proceeds via backside attack by the carbonyl oxygen of the carbamate group on the carbon bearing the arenetellurinyl group, followed by fission of the ethyl oxygen bond (Scheme 2). The reaction not only constitutes a simple (one pot),




Scheme 2.

direct method for the synthesis of 2-oxazolidinones from alkenes, but also indicates the good leaving ability of arenetellu- rinyl group.[6] Such versatility of tellurinyl function has prompted us to explore further its synthetic applicability and we found successfully amidotellurinylation of alkenes as well as one-pot formation of 2-oxazolines induced by it. Amidotellurinylation is accomplished at room temperature by a combination of the tellurinyl reagents ((1a) and $CF_3CO_2H$ or its anhydride), one equivalent $BF_3•OEt_2$, and acetonitrile acting both as a solvent and as a nucleophile, which is reminiscent of

Ritter amido synthetic reaction. The reaction gives Markovnikov type trans adducts, N-(β-aryltellurinylalkyl)acetamides, after reduction with hydrazine hydrate in EtOH.[7] A mechanism of the reaction is presented in Scheme 3. The initial amidotellurinylation starts with anti addition in a Markovnikov fashion via epioxytelluronium intermediate. It is followed by hydrolysis to iminol and then tautom-




Scheme 3.

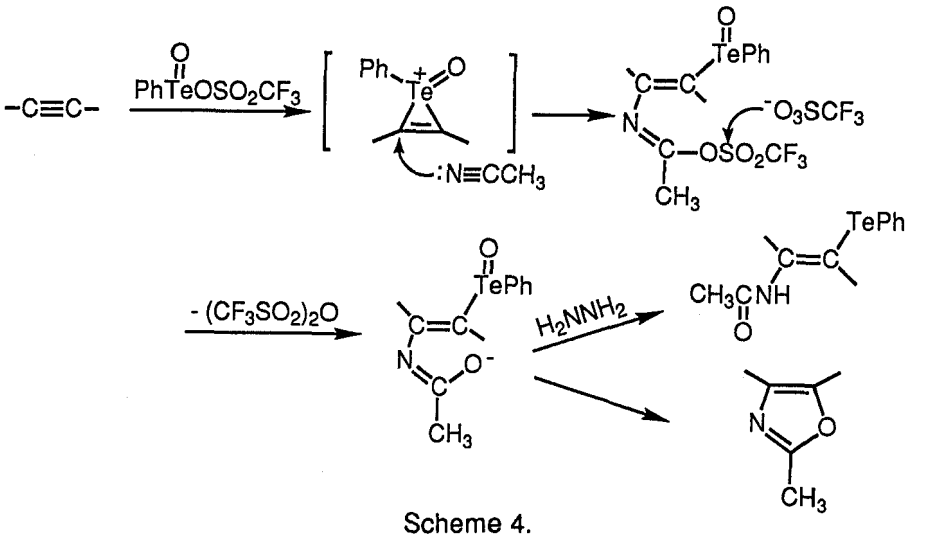
erization to amide. On the other hand, the formation of 2-oxazoline arises from intramolecular nucleophilic substitution in iminol at higher temperature, in which an inversion takes place at the carbon bearing the tellurinyl group. As a result, the net transformation of alkenes into oxazolines proceeds with Markovnikov regioselectivity and cis stereoselectivity. We have also succeeded in synthesis of 2-amino-2-oxazoline derivatives by the similar reaction of olefins with ethyl cyanocarbamate.[8] 2-Oxazolines are important heterocycles with various industrial applications, as well as of synthetic utility as a masked carbonyl group. There have been many ways in which 2-oxazolines may be formed, but this one-pot reaction offers the most facile synthetic method. It has thus turned out that a tellurinyl function has a

strong potential for developing new organic syntheses. Very recently we have found that arenetellurinic anhydrides (1a, b, c) were converted into their mixed anhydrides (2, 3, 4) by reactions with

ArTe(=O)X: 2, X=$CH_3CO_2$; 3, X=$CF_3CO_2$; 4, X=$CF_3SO_3$

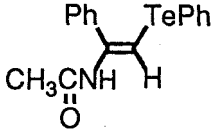
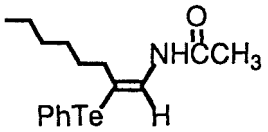
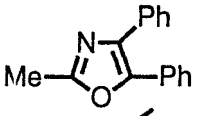
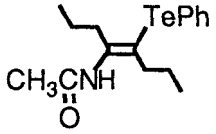
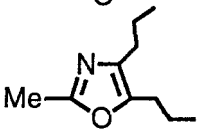
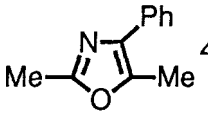
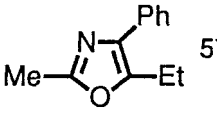
the corresponding counter acids or anhydrides in $CHCl_3$ or $CH_2Cl_2$. We succeeded in isolation as well as characterization of some of them as crystals and confirmed that they are real active reagents for the electrophilic additions.[9]

Very recently we have also started to study the reaction of acetylenes with the mixed anhydrides in acetonitrile. Preliminary results are shown in Table 1.[10] Terminal acetylenes undergo amidotellurinylation with 4a under the acid catalysis just like as olefins do and afford β-phenyltelluro vinyl acetamides after reduction, though the yields are not high yet. The regiochemistry of addition reaction of 1-octyne indicated by NMR spectroscopy is different from that of phenylacetylene. In the former case phenyltelluro group is added to the inner carbon of terminal acetylene bond and the reverse situation occurs in the latter one. In the case of internal actylenes, 2-methyl-4,5-disubstituted-1,3-oxazoles are obtained always as a major product and an amidotellurinylated adduct is isolated in some case as a by-product. Although the real mechanism is not clear at present, we assume a trans addition to the acetylenic bond via phenyl oxotellur-




Scheme 4.

Table 1 Reactions of acetylenes with $PhTe(=O)OSO_2CF_3$ ( 4a ) in $CH_3CN$.

| Run | Substrate | Additive | Conditions | Product [a] Addition compound | Yield / % | Cyclization compound | Yield / % |
|---|---|---|---|---|---|---|---|
| 1 | PhC≡CH | ----- | r.t. 12 h |  | 6 | | |
| 2 | | ----- | reflux 12 h | | 16 | | |
| 3 | | $BF_3 \cdot OEt_2$ | r.t. 12 h | | 13 | | |
| 4 | | $H_2SO_4$ | r.t. 12 h | | 38 | | |
| 5 | | $CF_3SO_3H$ | reflux 2 h | | 43 | | |
| 6 |  | $H_2SO_4$ | r.t. 12 h |  | 20 | | |
| 7 | | $CF_3SO_3H$ | 50 °C 2 h | | 28 | | |
| 8 | PhC≡CPh | $H_2SO_4$ | reflux 1 h | | |  | 57 |
| 9 | | $CF_3SO_3H$ | reflux 2 h | | | | 75 |
| 10 |  | $CF_3SO_3H$ | 50 °C 2 h |  | 23 |  | 57 |
| 11 | PhC≡CMe | $CF_3SO_3H$ | reflux 2 h | | |  | 44 |
| 12 | PhC≡CEt | $CF_3SO_3H$ | reflux 2 h | | |  | 57 |

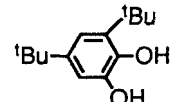
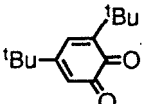
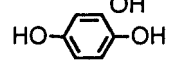
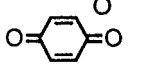
a) The product was isolated after treatment with $H_2NNH_2$ in $CH_3OH$

irene cation and cyclization of the amidotellurinylated product via a net trans substitution of phenyltellurinyl group by the imminol form of acetamide group (Scheme 4). The reason of absence of cyclized product in the reaction of terminal acetylenes is not clear at present. Although much work has to be done in future, the present reaction constitutes a novel as well as simple (one-pot) synthetic method of substituted 1,3-oxazoles.

The mixed anhydrides are soluble in usual organic solvents such as $CHCl_3$ or $CH_2Cl_2$. We examined their reactivities toward various functional groups in usual organic solvents to expand their applicabilities in organic synthesis.[11] The mixed anhydrides are inert to alcohol, phenol, and amine but reactive to thiol, phosphine, acyloin, α-hydroxy ester, catechol, and hydroquinone as summarized in Table 2. Any reagent can smoothly oxidize thiophenol and $Ph_3P$ to PhSSPh and $Ph_3PO$, respectively, at room temperature. The exact stoichiometry of the reagent is 1/3 mole per PhSH and 2/3 mole per $Ph_3P$, and it is reduced almost quantitatively to PhTeTePh. A plausible mechanism for the degradation of 2a is proposed in Scheme 5, which proceeds via reduction to benzenetellurenyl acetate followed by disproportionation to 2a and PhTeTePh.



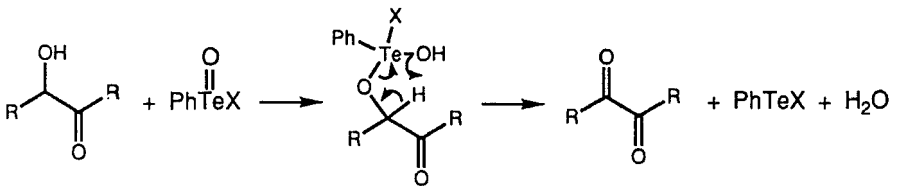
Table 2 Oxidative reactions with benzenetellurinic mixed anhydrides 2-4.

| Run | Substrate | Solvent | Temp | Time/h | Product | Isolated yield/% 2a | 3a | 4a |
|---|---|---|---|---|---|---|---|---|
| 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)$CO_2$Me | PhH | Reflux | 12 | PhCO$CO_2$Me | 59 | 76 | trace |
| 6 |  | $CHCl_3$ | Reflux | 12 |  | 40 | 18 | trace |
| 7 |  | $CHCl_3$ | Reflux | 24 |  | 38 | 28 | 0 |

$$PhTe(O)OCOCH_3 \longrightarrow PhTeOCOCH_3 + [O]$$
$$3PhTeOCOCH_3 \longrightarrow PhTe(O)OCOCH_3 + PhTeTePh + (CH_3CO)_2O$$

Scheme 5.

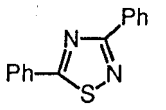
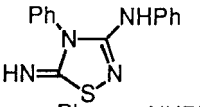
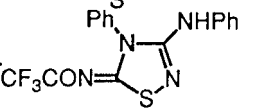
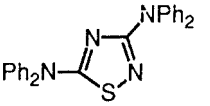
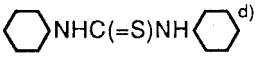
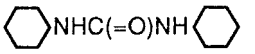
The oxidation of hydroxy compounds with the mixed anhydrides depends on both of the substrate and the reagent. Thus, 3a readily oxidized benzoin to benzil at room temperature, valeroin and methyl mandelate to 5,6-decanedione and phenyl glyoxylate in refluxing $CHCl_3$ and $C_6H_6$, respectively. It also oxidized catechol and hydroquinone to the corresponding quinones, though the conversion efficiency was very low. On the other hand, 2a was less reactive towards the former substrates but more reactive to the latter ones. Furthermore, 4a was quite inactive to all the substrates. The oxidations of the hydroxy compounds proceed probably via Te(IV) adduct (Scheme 6). Since such hypervalent species are stabilized by electron withdrawing ligands, the inactivities of 4a are ascribable to high stabilization of its adducts.



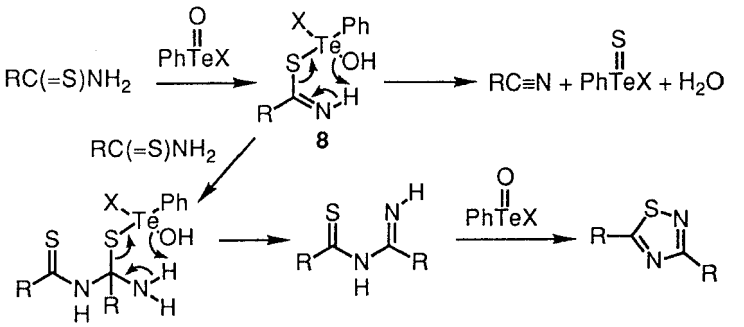

Scheme 6.

The reactions of 2a, 3a, and 4a with thioamides and thioureas were highly chemoselective. As shown in Table 3, 2a effected predominantly elimination reaction of thiobenzamide, phenylthiourea, N,N-diphenylthiourea to the corresponding nitriles, whereas 4a favored oxidative dimerization to 1,2,4-thiadiazole derivatives. Reagent 3a showed double-faced selection, i.e., thiobenzamide to benzonitrile and thiourea to the thiadiazole. A resonable mechanism for transformations into the two products is shown in Scheme 7. The selectivity again depends on reactivity of the hypervalent Te(IV) adduct formed from substrate and mixed anhydride. Thus the ready elimination directly leads to nitrile, otherwise dimerization occurs, finally leading to 1,2,4-thiadiazole. Furthermore, 2a and 3a could convert symmetrical N,N'-disubstituted thioureas into the urea derivatives as the main products. In contrast, 4a hardly gave such product. These differences in reactivity are difficut to explain clearly at the present stage of research but seem to be related to stability of the hypervalent Te(IV) adduct.

Table 3 Selective reactions depending on mixed anhydrides 2-4.

| Run | Substrate | Product | Yield/% | | |
|---|---|---|---|---|---|
| | | | 2a | 3a | 4a |
| 1 | $PhC(=S)NH_2$ [a] | PhC≡N | 80 | 68 | trace |
| | |  | 0 | 20 | 71 |
| 2 | $PhNHC(=S)NH_2$ [b] | PhNHC≡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 |  [d] |  | 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.



Scheme 7.

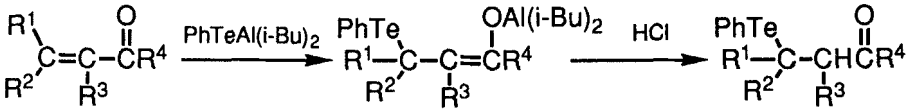
REACTIONS OF DIISOBUTYLALUMINUM BENZENETELLUROLATE (5)

The title compound (5) is a complex reagent composed of hard acid part ($i$-$Bu_2Al$) and soft base moiety (PhTe), and is expected to exhibit very unique as well as interesting reactivities, for instance oxophilicity. After several unsuccessful attempts we have observed that 5 is conveniently prepared by treatment of PhTeTePh with double the quantity of diisobutylaluminum hydride in THF at room temperature for 0.5 hour under an argon atmosphere. The completion of the conversion is ascertained by a theoretical amount of hydrogen gas evolution (Scheme 8).[12] The reagent 5 is so highly sensitive to air and moisture that it is

$$\mathrm{PhTeTePh} + 2(i\text{-}Bu)_2AlH \longrightarrow 2(i\text{-}Bu)_2AlTePh + H_2$$

Scheme 8. (5)

used in situ like the other aluminum chalcogens for further reaction. When α,β-unsaturated carbonyl compounds are allowed to react with a colorless THF solution of 5 at -78°C, 1,4-conjugate addition occurs smoothly for 0.5 hour and β-phenyltelluro carbonyl compounds are obtained after quenching with a degassed dilute aqueous HCl at the same temperature (Scheme 9).



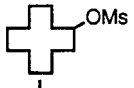
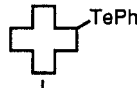
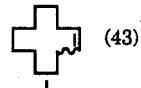
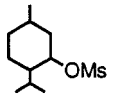
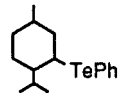
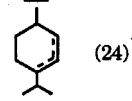

Scheme 9.

Terminal and cyclic enones are converted to the corresponding β-phenyltelluro ketones in fair to good yields. Alkyl substituents on the double bond lead to a lowering of the reactivity owing to steric and electronic effects. Conjugated enals also give 1,4-adducts, but the yields are moderate probably because of competitive 1,2-addition to the formyl group. It is well recognized that aluminum enolates are highly potential agents for aldol reaction. The aluminum enolates derived from the present conjugate addition to α,β-unsaturated cyclic ketones also undergo aldol reaction with aldehyde in THF at -78 to -30°C for 3 hours to give α-hydroxyalkyl carbonyl compounds in good yields. The synthetic potentiality of the present aldol product bearing a phenyltelluro group at β-position is successfully utilized by its conversion into telluroxide-elimination product on treatment with

m-chloroperbenzoic acid. The overall transformation therefore provides α-hydroxyalkylation of α,β-unsaturated carbonyl compound.[12] We further explored the reactivity of 5 towards various functional groups to extend its synthetic applicability.[13] When 5 is treated with 1-methoxybutane in $CH_2Cl_2$ at room temperature, a substitution proceeds slowly and forms methyl phenyl telluride as a sole product in 14% yield after 24 hours, whereas no substitution product is obtained by the treatment of 1-bromooctane with 5 under the same conditions. This obviously indicates the specific reactivity of 5 to oxygen functional groups. The high reactivity is demonstrated by nucleophilic reactions to acetals and alkyl sulfonates. Aldehyde dimethyl acetals are smoothly converted to monotelluroacetals, and under forced conditions with excess 5, to the corresponding ditelluroacetals. The nucleophilic substitutions of alkyl methanesulfonates and p-toluenesulfonates proceed at 0°C or below, in contrast to a similar reaction with sodium benzenetellurolate, which requires heating at reflux temperature of EtOH-THF (1:1). Primary alkyl sulfonates are converted to alkyl tellurides in high yields, whereas sec-alkyl methanesulfonates give both sec-alkyl tellurides and olefins, β-elimination products, even at sufficiently low temperature. This indicates the $S_N2$-type nucleophilicity and basicity of 5 (Table 4). These reactions are markedly retarded in THF, which solvates aluminum species, suggesting that C-O bond activation by the coordination of the oxygen to 5 is important to smooth reactions.

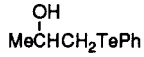
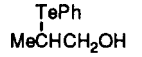
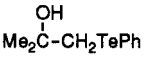
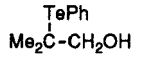
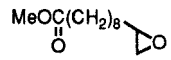
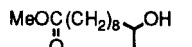
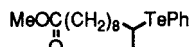
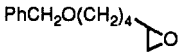
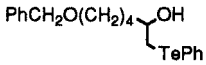
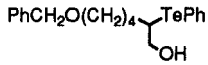
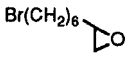
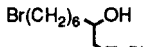
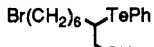
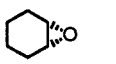
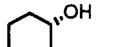
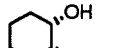
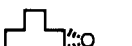
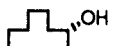
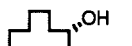
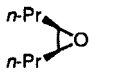
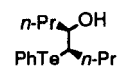
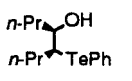
The high reactivity of 5 toward oxygen functional groups was also substantiated by the ready reactions with oxiranes under neutral conditions. As shown in Table 5, the nucleophilic ring opening of mono-, 2,2-di-, and cis-2,3-di-substituted oxiranes proceeds at room temperature to afford β-hydroxytellurides in high yields and tolerates the coexistence of the ester, ether, and halide groups. The ring opening is highly regiospecific as demonstrated in the predominant formation of primary alkyl tellurides from monosubstituted and gem-disubstituted oxiranes. Moreover, cis-2,3-disubstituted oxiranes give stereospecific ring-opening products, threo-β-hydroxytellurides, by the $S_N2$ reaction. On the other hand, the ring opening of trans-disubstituted and trisubstituted oxiranes competes with isomerization to allylic alcohols as

Table 4 Reactions of acetals and alkyl sulfonates with 5 in dichloromethane.

| Run | Substrate | Temp/°C | Time/h | Product (Isolated yield/%) |
|---|---|---|---|---|
| 1 | $CH_2(OCH_3)_2$ | r t | 7 | $CH_3OCH_2TePh$ (42) |
| 2 | $CH_3(CH_2)_{10}CH(OCH_3)_2$ | r t | 3 | $CH_3(CH_2)_{10}CHOCH_3$ (80) <br> TePh |
| 3[a] | $CH_3(CH_2)_{10}CH(OCH_3)_2$ | reflux | 24 | $CH_3(CH_2)_{10}CH(TePh)_2$ (50) |
| 4 | $CH_3(CH_2)_5OMs$ | 0 | 2 | $CH_3(CH_2)_5TePh$ (72) |
| 5 | $CH_3(CH_2)_5OTs$ | 0 | 3 | $CH_3(CH_2)_5TePh$ (72) |
| 6 | $Ph(CH_2)_3OMs$ | 0 | 1 | $Ph(CH_2)_3TePh$ (84) |
| 7 | $CH_3CH(CH_2)_5CH_3$ <br> OMs | -15 | 4 | $CH_3CH(CH_2)_5CH_3$ (54) <br> TePh |
| 8 |  | -40 | 5.5 |  (46)  (43)[b] |
| 9 |  | 0 | 2.5 |  (42)  (24)[b] |

a) Excess 5 (2.5-fold the molar quantity) was used. b) Determined by GLC analysis.

Table 5 Reactions of mono-, 2,2-di-, and cis-2,3-di-substituted oxiranes with 5[a].

| Run | Substrate | Time/h | Product | | Yield/% (Ratio)[b] |
|---|---|---|---|---|---|
| 1 |  | 3 |  |  | 88 (94:6) |
| 2 |  | 3 |  |  | 64 (99>1) |
| 3 |  | 2 |  |  | 72 (97:3) |
| 4 |  | 2 |  |  | 70 (97:3) |
| 5 |  | 2 |  |  | 59 (87:13) |
| 6 |  | 4.5 |  |  | 80 (93:7) |
| 7 |  | 1.5 |  |  | 79 (99>1) |
| 8 |  | 1.5 |  |  | 71 (99>1) |

a) The reactions were carried out in dichloromethane at room temperature. b) Determined by $^{13}C$ NMR analysis.

summarized in Table 6. The formation of allylic alcohols, though it is supressed in a concentrated solution or in THF, precedes the ring opening when the $S_N2$ attack is sterically hindered. Moreover, 5 preferentially abstracts α-proton of alkyl group located on the less hindered side of oxirane group. These results support that the isomerization to allylic alcohols proceeds via a cyclic syn-elimination mechanism involving the coordination of oxirane to 5 as illustrated in Fig. 1.

In conclusion, these unique oxygenophilic reactivities of 5 are attributable to high polarizability of Te-Al bond induced by coordination of the oxygen in a substrate to the aluminum site.

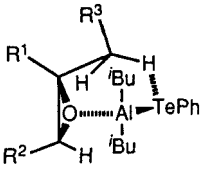
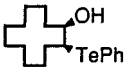
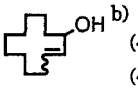
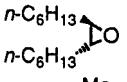
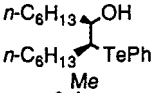
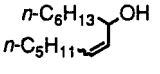
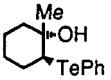
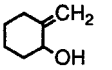
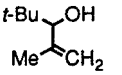


Fig. 1.

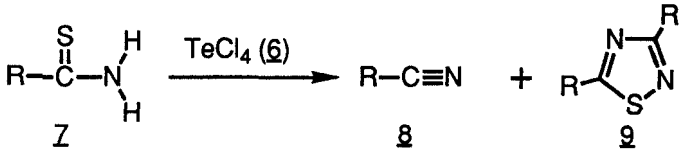
Table 6 Reactions of trans-2,3-disubstituted and trisubstituted oxiranes with 5 [a]

| Run | Substrate | Solvent | Time/h | Product (Isolated yield/%) | | | |
|---|---|---|---|---|---|---|---|
| 1 |  | hexane | 2 |  | (47) |  [b] | (42) |
| 2 | | $CH_2Cl_2$ | 2 | | (40) | | (48) |
| 3 [c] | | $CH_2Cl_2$ | 2 | | (60) | | (32) |
| 4 | | THF | 24 | | (35) | | (8) |
| 5 |  | $CH_2Cl_2$ | 2 |  | (80) |  | (3) |
| 6 |  | $CH_2Cl_2$ | 2 |  | (62) |  | (18) |
| 7 |  | $CH_2Cl_2$ | 2 | ——— | |  | (76) |

a) The reactions were carried out at room temperature. b) E/Z = 2/1 by $^{13}C$ NMR analysis.
c) In a fivefold-concentrated solution compared to that of Run 2.

REACTIONS OF $TeCl_4$ (6) WITH THIOAMIDES AND RELATED COMPOUNDS

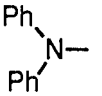
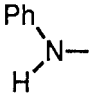
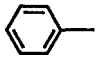
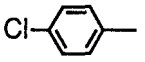
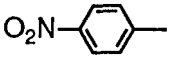
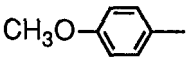
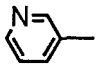
Tellurium tetrachloride (6) is a commercially available reagent containing tetravalent Te and expected to behave as a Lewis acid and a soft electrophile in organic reactions. We have investigated its reaction with thioamides (7) and related compounds (Scheme 10).[14]



7 8 9 Scheme 10

In chloroform 1,1-diphenylthiourea (7, R = $NPh_2$) affords a thiadiazole (9, R = $NPh_2$), an oxidative dimerization product, in preference to diphenylcyanamide (8, R = $NPh_2$), though the yields are low (9 and 13% at room and reflux temperatures, respectively). When a strong amine base, such as $Et_3N$ or DBN, is added to the reaction mixture, dehydrosulfurization occurs selectively and smoothly to afford the nitrile in a good yield. Weaker bases, such as pyridine or $CH_3CO_2Na$, tend to decrease the yield. Thus, the reactions of various thioamides with 6 in the presence of $Et_3N$ afford the corresponding nitriles selectively in good yields (Table 7).

Table 7 Dehydrosulfurization reaction of 7 to 8 with 6 in the presence of $Et_3N$.

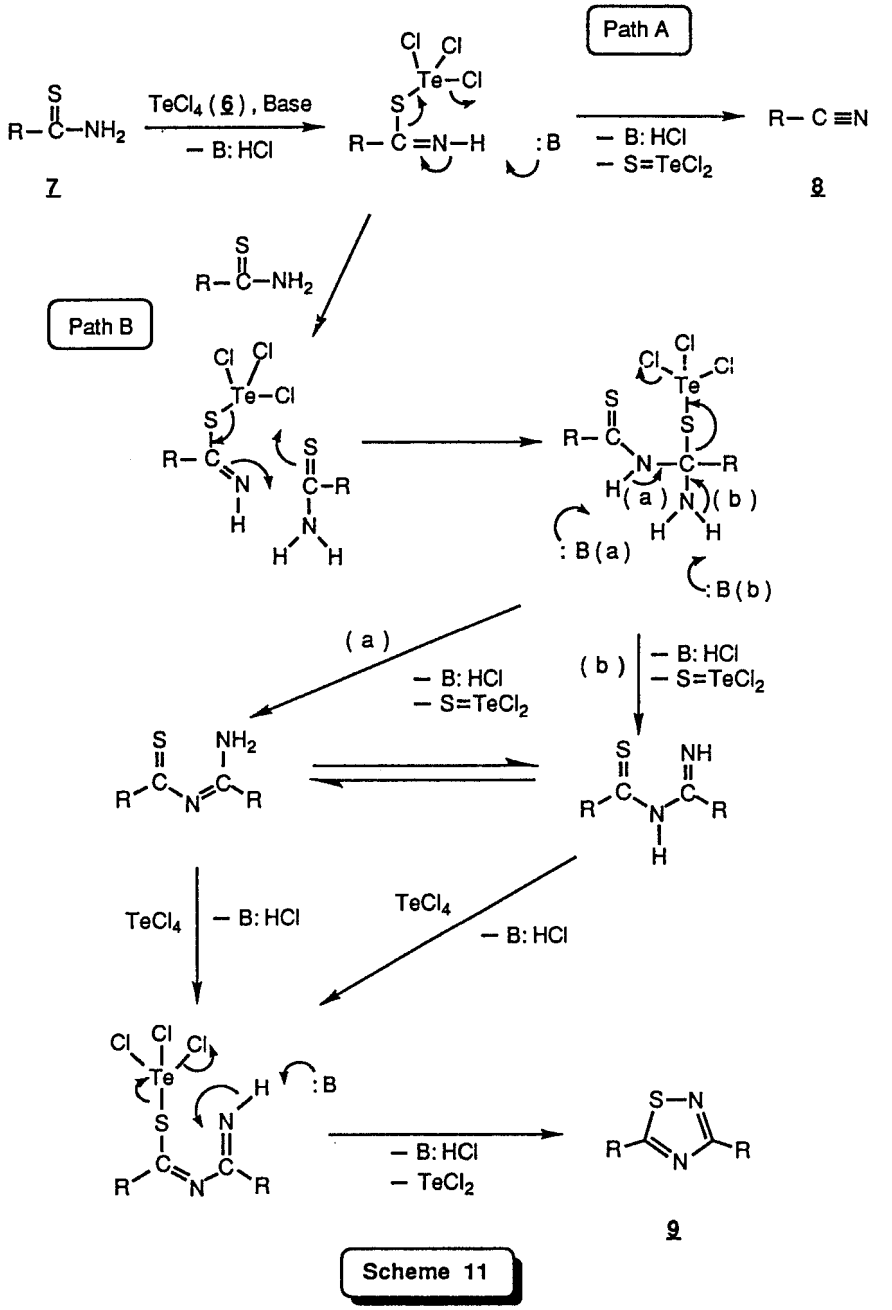
| Run | R | Temp / °C | Yield / % |
|---|---|---|---|
| 1 |  | RT | 78 |
| | | 50 | 84 |
| 2 |  | RT | 57[a] |
| | | 50 | 67[a] |
| 3 |  | RT | 92[b] |
| 4 |  | RT | 81 |
| 5 |  | RT | 86 |
| 6 |  | RT | 83 |
| 7 |  | RT | 80 |

a) The product contained triazine which was formed by trimerization of phenylcyanamide.

b) GC yield.

To explain the product selectivity in the present reactions, a tentative mechanism is proposed as shown in Scheme 11. The elimination reaction (Path A) precedes under the strongly basic conditions to lead to nitriles, while the oxidative dimerization reaction (Path B) occurs

preferentially under the nonbasic conditions to yield 9. A tellurium derived product in the present reaction, $S{=}TeCl_2$, seems to regenerate $TeCl_4$ (6) partly by disproportionation after desulfurization.




Scheme 11

Acknowledgement

The present work was in part supported by the Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No.03233101 and the Grant-in-Aid for Co-operative Research (A) No. 02303012 from the Ministry of Education, Science and Culture, Japan.

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