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CYCLOFUNCTIONALIZATION OF HYDROXYOLEFINS INDUCED BY ARENETELLURINIC ANHYDRIDE1)

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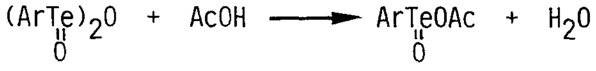
Abstract: Arenetellurinic anhydride reacts with hydroxyolefins in acetic acid at reflux to give cyclic ethers bearing a phenyltelluro group. A mechanism via intramolecular oxytellurinylation with arenetellurinyl acetate is proposed.

A number of organoselenium reagents are utilized as efficient initiators of ring closures leading from unsaturated substances to heterocycles.2) These cyclizations have the advantage of being applicable to complex natural product syntheses. On the other hand, such cyclofunctionalization using tellurium species has not been studied in detail, though organic syntheses on tellurium-based methodology have become increasingly important.3) Only two literatures on it are now known. Petragnani et al. reported the lactonization of γ- and δ-unsaturated acids with aryltellurium mono and trihalides.4) Bergman and Engman reported the formation of bis-cyclic ethers on treatment of hydroxyolefins with tellurium dioxide in acetic acid containing lithium chloride.5) We now like to present novel cyclofunctionalization of hydroxyolefins as well as acetoxytellurinylation of olefins conveniently induced by arenetellurinic anhydride in acetic acid.6)

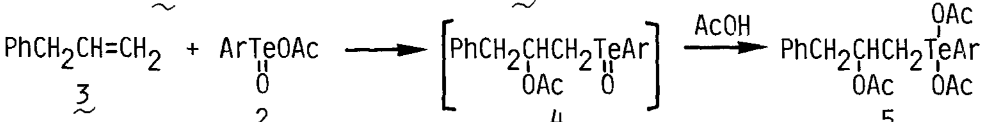
Arenetellurinic anhydride 1 has been recently recognized as a versatile oxidizing agent for thiols, phosphines, thioamides, thioureas, thionoesters, benzylic alcohols, and hydroquinones.7,8) In addition, it acts as a selective catalyst for the hydration of terminal alkynes in acetic acid at reflux.7) Sonoda et al. showed that benzenetellurinic anhydride 1 (Ar=Ph) oxidized olefins in acetic acid at reflux leading to vic-diacetates, which was accelerated by a catalytic amount of sulfuric acid.9) This diacetoxylation was proposed to proceed via acetoxytellurenylation of olefin with benzenetellurenyl acetate (PhTeOAc) generated from 1, followed by acetolysis of phenyltelluro group.

We have, however, found that p-methoxybenzenetellurinic anhydride 1



$$(\mathrm{Ar}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{Te}})_2\mathrm{O} + \mathrm{AcOH} \longrightarrow \mathrm{Ar}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{Te}}\mathrm{OAc} + \mathrm{H_2O}$$

1 2

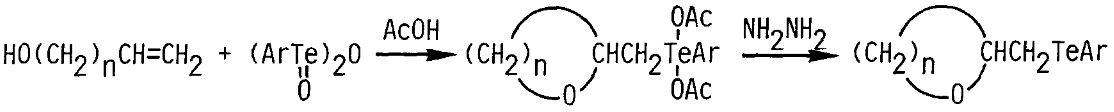


$$\mathrm{PhCH_2CH{=}CH_2} + \mathrm{Ar}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{Te}}\mathrm{OAc} \longrightarrow \left[\mathrm{PhCH_2}\underset{\mathrm{OAc}}{\mathrm{CH}}\mathrm{CH_2}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{Te}}\mathrm{Ar}\right] \xrightarrow{\mathrm{AcOH}} \mathrm{PhCH_2}\underset{\mathrm{OAc}}{\mathrm{CH}}\mathrm{CH_2}\overset{\mathrm{OAc}}{\underset{\mathrm{OAc}}{\mathrm{Te}}}\mathrm{Ar}$$

3 2 4 5

(Ar=p-MeOC$_6$H$_4$) reacted with allylbenzene **3** in acetic acid at reflux for 15 hrs to give, together with unreacted **3**, tellurium compound **5** (40%) rather than vic-diacetate. Since telluroxide is readily convertible into tellurium diacetate in acetic acid,[10] it is assumed that p-methoxybenzenetellurinyl acetate **2** (Ar=p-MeOC$_6$H$_4$) is the real active species and undergoes acetoxytellurinylation with allylbenzene **3**. Compound **2** is also postulated as the real catalyst for the hydration of terminal alkynes above stated.[7] The formation of **2** was actually confirmed on separately heating **1** in acetic acid.[11] It was a very hygroscopic oily material, which showed the following spectral data; IR (neat) 1712 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ 1.90(s, 3H, OAc), 3.78(s, 3H, OMe), 6.86(ABd, 2H, ArH), 7.76(ABd, 2H, ArH).

We felt that, if an effective nucleophilic group was present at the suitable position of the olefinic molecule, an intramolecular cyclization instead of acetoxylation might occur. Thus, treatment of hydroxyolefins **6** with p-methoxybenzenetellurinic anhydride (1.1 eq) in acetic acid at reflux for 15 hrs gave cyclic ethers **7** bearing a tellurium functional group. Benzenetellurinic anhydride and β-naphthalenetellurinic anhydride behaved similarly. Because of hygroscopic, intractable materials, compound **7** were isolated as the corresponding tellurides **8** after reduction with hydrazine hydrate in ethanol at 60°C for 20 min.



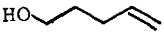
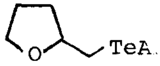
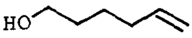
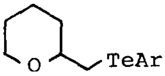
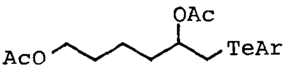
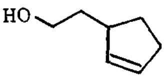
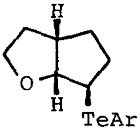
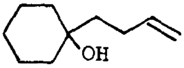
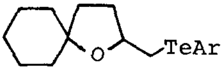
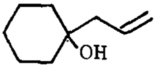
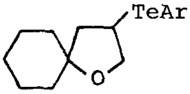
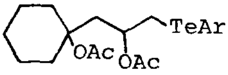
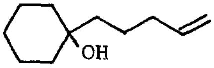
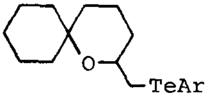
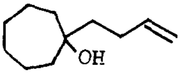
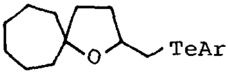
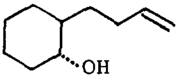
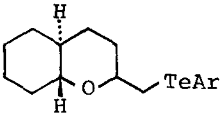
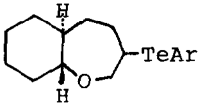
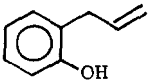
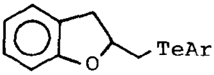
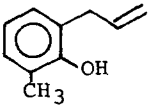
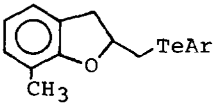
6 **1** **7** **8**

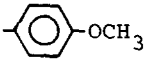
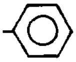
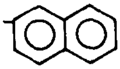
Table 1 summarizes a variety of examples which exhibit some features of the oxytellurinylation. Thus, the addition is highly regioselective, obeying Markovnikov rule, and stereoselective and anti on the basis of the stereochemistry of the bicyclic product in Run 3. The five-membered cyclic ether is generally easier to form than the other rings. Especially, the cyclization of o-allylphenols to benzofuran derivatives proceeds in excellent yields. The example of Run 5 demonstrates that the five-membered ring is favorable over the four-membered one in spite of anti-Markovnikov addition. An attempted formation of three- or four-membered ring from allyl alcohol was unsuccessful. As shown in Runs 2 and 5, sluggish cyclization often competes with acetoxylation.

Since there have been so far developed a number of chemical modifications of phenyltelluro group such as reductive detelluration,[12] oxidative elimination,[13] halogenolysis,[14] and methanolysis,[15] we believe the present cyclization reaction provides a useful new approach to various cyclic compounds.

Acknowledgement: The authors wish to express their thanks to the Nitto Chemical Industrial Co., Ltd. for the financial aid.

Table 1. Reactions of hydroxyolefins with arenetellurinic anhydride $\underset{\sim}{1}$ in acetic acid at reflux for 15 hrs

Run	Substrate	Product	Yield/%
1			80[a], 77[b], 73[c]
2			38[a], 26[c]
			26[a], 23[c]
3			42[a], 53[c]
4			86[a]
5			15[a]
			29[a]
6			90[a]
7			94[a]
8			45[a]
			22[a]
9			94[a], 92[c]
10			90[a]

a: Ar=  b: Ar=  c: Ar= 

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