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TELLURIUM-BASED ORGANIC SYNTHESIS: A NOVEL ONE-POT FORMATION OF 2-OXAZOLINES FROM ALKENES INDUCED BY AMIDOTELLURINYLATION

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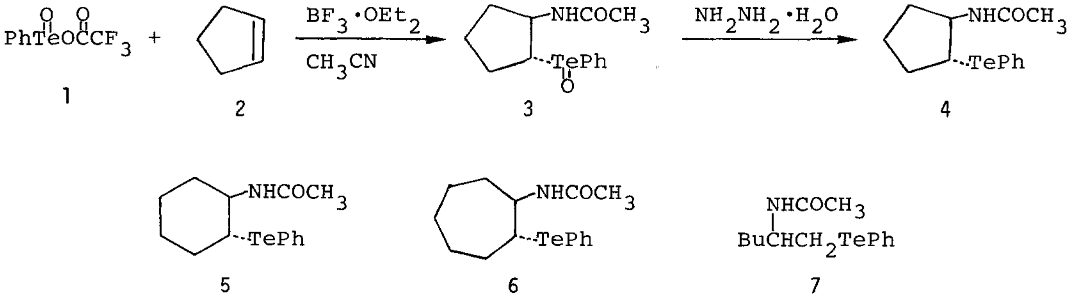
Abstract: Benzenetellurinyl trifluoroacetate readily reacts with alkenes in acetonitrile in the presence of boron trifluoride etherate at 75 °C to give 2-oxazolines via amidotellurinylation.

Organic syntheses on tellurium-based methodology have become increasingly important.[1)] One point of the strategy is to develop a convenient method for introducing a tellurium function into organic substrates. The addition reactions of unsaturated compounds with tellurium (IV) species serve for this purpose.[2)] We recently found that benzenetellurinyl trifluoroacetate (1) in combination with alcohol or carbamate as a nucleophile readily effected oxytellurinylation or aminotellurinylation towards alkenes.[3)] In addition, the latter product, β-phenyltellurinyl carbamate did not effect any telluroxide elimination[4)] but an unexpected intramolecular cyclization at high temperature to give 2-oxazolidinone.[5)] This reaction not only constitutes a simple, direct method for the synthesis of 2-oxazolidinones but also indicates the good leaving ability of the tellurinyl group. Such versatility of tellurinyl functuion has prompted us to explore further its synthetic application. Here we wish to present successful amidotellurinylation of alkenes as well as one-pot formation of 2-oxazolines induced by it.

Amidotellurinylation was accomplished by a combination of the tellurinyl reagent (**1**) and acetonitrile acting both as a solvent and as a nucleophile, which is reminiscent of Ritter amido synthesis.[6)] Thus, cyclopentene (**2**) was treated with **1** in acetonitrile at room temperature for 12 h to give trans-N-

Scheme 1



[(2-phenyltellurinyl)cyclopentyl]acetoamide (**3**) which, after reduction with hydrazine hydrate in ethanol at 60°C, was isolated as telluride **4** in 89 % yield (Scheme 1). One equivalent boron trifluoride is required to promote the amidotellurinylation. Cyclohexene and cycloheptene similarly gave the corresponding tellurides **5** and **6** in 76 % and 92 % yields, respectively. 1-Hexene also gave an adduct **7** of Markovnikov type in 95 % yield. On the other hand, the same reactions at an elevated temperature of 65-75 °C produced 2-oxazoline derivatives in high yields.7) Table 1 summarizes a variety of examples, which demonstrate this reaction to proceed with high regioselectivity and stereoselectivity.8) For example, 1-hexene gave 4-substituted 2-oxazoline, and cis and trans 4-octenes gave cis and trans 4,5-disubstituted ones, respectively. In addition, propionitrile and benzonitrile were also effective as the nucleophiles, enabling the formation of the corresponding 2-ethyl or phenyl derivatives. The less nucleophilicity of benzonitrile resulted in a lowering of the yield due to competitive side reactions at 75°C. However, it was considerably improved by taking a longer reaction time at 65°C.

A mechanism for the formation of 2-oxazolines from alkenes is presented in Scheme 2. The initial amidotellurinylation starts with anti addition in a Markovnikov fashion via epoxytelluronium intermediate **8**. It is followed by hydrolysis of adduct **9** to iminol **10**9) and then tautomerization to amide **11**. On the other hand, the formation of 2-oxazoline **12** arises from an intramolecular nucleophilic substitution in iminol **10** at higher temperature, in which a configurational inversion takes place at the carbon bearing the tellurinyl group. As a result, the net transformation of alkenes into oxazolines proceeds with Markonikov regioselectivity and cis stereoselectivity.

2-Oxazolines are an important heterocycle with various industrial applications,10) as well as of synthetic utility as a masked carbonyl group.11) There have been many ways in which 2-oxazolines may be formed, but

Scheme 2

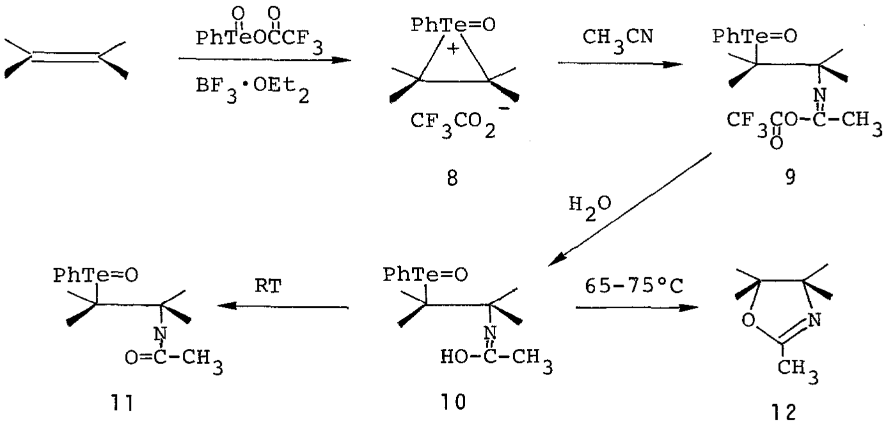
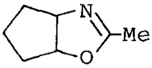
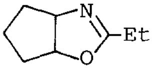
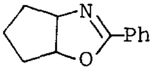
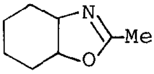
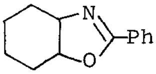
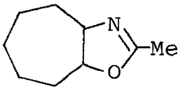
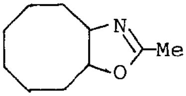
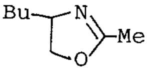
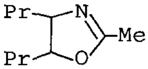
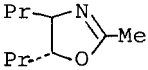
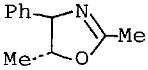


Table 1. Formation of 2-oxazolines from alkenes with benzenetellurinyl trifluoroacetate in the presence of boron trifluoride etherate

Run	Substrate	Conditions			Product	Yield/%
		Solvent	Temp/°C	Time/h		
1	cyclopentene	MeCN	75	3		95
2	cyclopentene	EtCN	75	3		96
3	cyclopentene	PhCN	75 65	3 12		46 87
4	cyclohexene	MeCN	75	8		80
5	cyclohexene	PhCN	75 65	3 12		34 53
6	cycloheptene	MeCN	75	3		97
7	cyclooctene	MeCN	75	3		29
8	1-hexene	MeCN	75	3		96
9	cis-4-octene	MeCN	75	3		83
10	trans-4-octene	MeCN	75 65	3 8		33 56
11	trans-β-methyl-styrene	MeCN	75	3		71

the present 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.

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7) A typical experimental procedure is as follows. Benzenetellurinyl trifluoroacetate **1** was in situ generated by treatment of benzenetellurinic anhydride (0.270 g, 0.59 mmol) with trifluoroacetic acid (0.159 g, 1.4 mmol) in 6 ml of acetonitrile at room temperature for 10 min. Into the solution were successively added cycloheptene (0.096 g, 1.0 mmol) and boron trifluoride etherate (0.20 g, 1.4 mmol). The mixture was heated at 75 °C for 3 h, and gradually turned black red. It was cooled to room temperature, poured into 25 ml of chloroform, and then extracted with 0.5 N HCl (25 ml × 2). The extract was made alkaline by addition of NaOH pellets with ice cooling, and again extracted with ether (25 ml × 2). After dryness over anhyd. K_2CO_3, evaporation gave pure 2-methyl-4,5-pentamethylene-2-oxazoline (0.149 g) as a colorless oil with b.p. 130 °C/42 mmHg.

8) The stereochemistry of this reaction essentially resembles that for the preceding transformation of alkene into 2-oxazolidone, indicating a similar mechanism of addition/intramolecular substitution (ref. 5).

9) Water for hydrolysis is formed on the generation of benzenetellurinyl trifluoroacetate.

10) For excellent reviews on the preparations, reactions, and applications of oxazolines, see, J. A. Frump, Chem. Rev., 71, 483 (1971); R. H. Wiley and L. L. Bennett, Jr., Chem. Rev., 44, 447 (1949).

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