Organotellurium-mediated Synthesis of Oxazolidin-2-ones from Alkenes

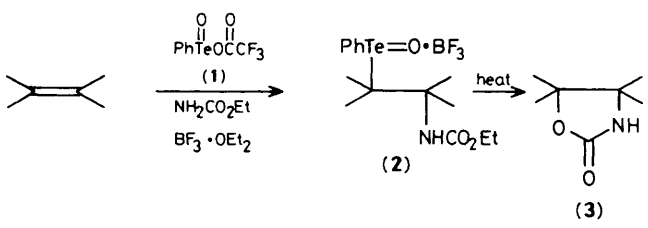
Nan X. Hu, Yoshio Aso, Tetsuo Otsubo, and Fumio Ogura*

Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Saijo, Higashi-Hiroshima 724, Japan

Phenyltellurinyl trifluoroacetate in combination with ethyl carbamate and boron trifluoride–diethyl ether reacted with alkenes in refluxed 1,2-dichloroethane, regio- and stereo-selectively giving oxazolidin-2-ones in high yields.

Oxazolidin-2-ones are an important class of heterocyclic compounds with wide application. The most common syntheses use as starting materials the corresponding *cis*-β-amino alcohols, which are often difficult to obtain.[1] The route from alkenes gives good yields, but requires a multi-step procedure. We present here a simple, direct synthetic method from alkenes mediated by an organotellurium species.

We recently found that phenyltellurinyl trifluoroacetate (**1**) in combination with ethyl carbamate effected aminotellurinylation of alkenes in refluxed dichloromethane or chloroform in the presence of $BF_3{\cdot}OEt_2$, to give β-phenyltellurinyl carbamate (**2**) (Scheme 1).[2] However, when the reaction was carried out at a higher temperature in refluxed 1,2-dichloroethane, the oxazolidin-2-one (**3**) was obtained in high yield instead of (**2**). Use of ethyl *N*-alkylcarbamates led to the formation of the *N*-alkyl derivative. A variety of examples in Table 1 demonstrate the reaction to be regio- and stereo-selective. Thus, terminal alkenes gave 4-substituted oxazolidin-2-ones, while *cis*- and *trans*-alkenes gave *cis*- and *trans*-4,5-

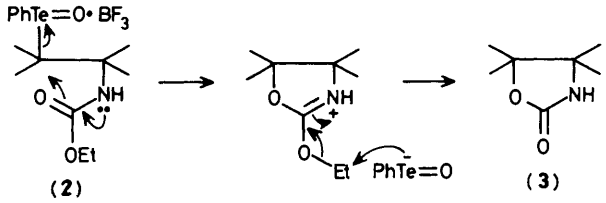


Scheme 1

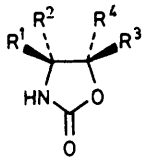
Table 1. Synthesis of oxazolidin-2-ones from alkenes.[a]

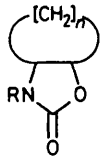
Substrate	Product	Yield/%[b]
Hex-1-ene	(**4**)+(**5**)[c]	91
Styrene	(**6**)	92
α-Methylstyrene	(**7**)	61
trans-β-Methylstyrene	(**8**)	79
trans-Oct-4-ene	(**9**)	53
cis-Oct-4-ene	(**10**)	84
Cyclopentene	(**11**)	92
Cyclohexene	(**12**)	86
Cyclohexene	(**13**)[d]	77
Cyclohexene	(**14**)[e]	76
Cycloheptene	(**15**)	81
Indene	(**16**)	79
1,2-Dihydronaphthalene	(**17**)	81

[a] Typical procedure: a mixture of alkene (1.0 mmol), phenyltellurinyl trifluoroacetate (0.55 mmol), ethyl carbamate (5.0 mmol), and $BF_3{\cdot}OEt_2$ (1.2 mmol) was refluxed in 1,2-dichloroethane (5 ml) for 6—20 h. [b] Yields of products isolated after chromatographic separation. [c] Isomeric ratio (**4**) : (**5**) = 75 : 25. [d] Ethyl *N*-methylcarbamate used instead of ethyl carbamate. [e] Ethyl *N*-ethylcarbamate used instead of ethyl carbamate.



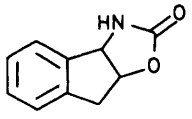
Scheme 2





(4) R^1 = Bu, $R^2 = R^3 = R^4$ = H
(5) $R^1 = R^2 = R^4$ = H, R^3 = Bu
(6) R^1 = Ph, $R^2 = R^3 = R^4$ = H
(7) R^1 = Ph, R^2 = Me, $R^3 = R^4$ = H
(8) R^1 = Ph, $R^2 = R^3$ = H, R^4 = Me
(9) $R^1 = R^4$ = Pr, $R^2 = R^3$ = H
(10) $R^1 = R^3$ = Pr, $R^2 = R^4$ = H

(11) n = 3, R = H
(12) n = 4, R = H
(13) n = 4, R = Me
(14) n = 4, R = Et
(15) n = 5, R = H



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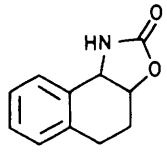

(17)

disubstituted ones, respectively. We suggest that the oxazolidinone (3) is formed by thermolysis of (2), as shown in Scheme 2. The initial aminotellurinylation reaction proceeds with high Markovnikov regioselectivity as well as *trans*-stereoselectivity, *via* an epitelluronium intermediate.[2] The conversion of (2) into (3) probably proceeds *via* backside attack by the carbonyl oxygen of the carbamate function on the carbon bearing the phenyltellurinyl group, followed by fission of the ethyl–oxygen bond. Therefore, the net addition to the alkene is *cis*-stereoselective. The latter cyclization step is reminiscent of pyrolysis of β-halogeno-carbamates to produce oxazolidinones.[3,4] The pyrolytic temperature (83 °C) for (2) is much lower than that for the β-halogeno-carbamates (120—200 °C), indicating the good leaving ability of the phenyltellurinyl group.

The reaction provides a simple, direct method for the synthesis of oxazolidin-2-ones from alkenes. In addition, it may be useful as providing stereoselective access to *cis*-β-amino alcohols from alkenes, oxazolidin-2-ones being readily converted into *cis*-β-amino alcohols by hydrolysis with alcoholic base.[4]

Partial financial support from the Nitto Chemical Industry Co., Ltd., and by a Grant-in-Aid for General Scientific Research (No. 62470023) from the Ministry of Education, Science and Culture is gratefully acknowledged.

Received, 18th May 1987; Com. 668

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