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IODO- AND PHENYLSELENOCARBAMATE CYCLIZATIONS: NEW VERSATILE METHODS FOR FUNCTIONALIZATION OF OLEFINIC BONDS

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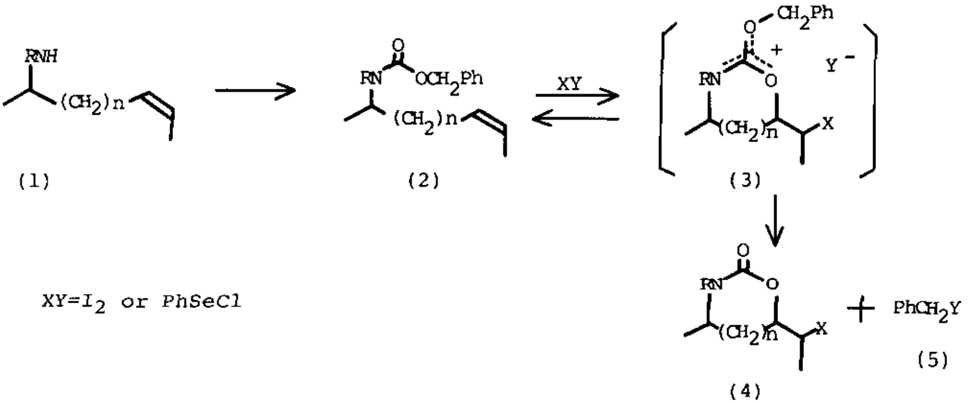
Abstract-----Efficient methods for conversion of the unsaturated benzyl carbamates (6-9) into the cyclic carbamates (11-14) have been developed.

In connection with investigations directed toward the syntheses of alkaloids such as histrionicotoxins,[1] we studied synthetic methods to construct cyclic carbamates from certain unsaturated amines as depicted in the following equations.

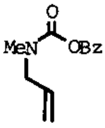
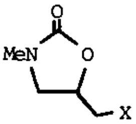
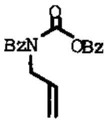
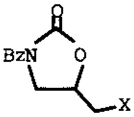
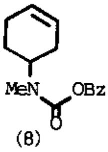
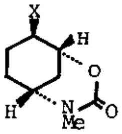
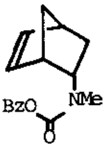
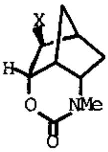


XY=I_2 or PhSeCl

We assumed that a carbamate (2) containing an olefin group at an appropriate position could be converted to a cyclic carbamate (4) <u>via</u> an oxonium intermediate (3) with simultaneous loss of the benzyl moiety under the halo- or phenylseleno-lactonization conditions,[2,3] since the similar type of the carbamate[4] and the amide[5-8] mediated cyclization has been precedented.

As summarized in Table, the benzyl carbamates (6-9), on treatment with an equimoler amount of iodine in methylene chloride at room temperature, furnished the cyclic carbamates (11a-14a) in excellent yields, respectively. Similarly, phenylselenyl chloride was found to be effective on this type of cyclization although much more forcing conditions (reflux in dichloroethane) were necessary[9] as compared to the iodocarbamate cyclization.

Table

Carbamate[a,10]	Cyclization Product[10]	Yield(%)[b]
 (6)	 (11a) X=I (11b) X=SePh	95 52
 (7)	 (12a) X=I (12b) X=SePh	96 48
 (8)	 (13a) X=I (13b) X=SePh	98 36
 (9)	 (14a) X=I (14b) X=SePh	92 88

a) The benzyl carbamates were prepared from the correspoding amines using carbobenzoxy chloride in usual manner.

b) isolated yield

As mentiond above, we have demonstrated that both iodine and phenylselenyl chloride can be used effectively to induce cyclization of unsaturated benzyl carbamates in a regio- and stereocontrolled manner. Now, application of this method to the synthesis of natural products is under investigation.

GENERAL PROCEDURE

Iodocarbamate Cyclization-----To a stirred solution of the benzyl carbamate (0.2 mmol) in methylene chloride (1 ml) at room temperature under argon was added iodine (0.21 mmol). After 2.5 h, the reaction mixture was diluted with methylene chloride, washed with 1% aq. $Na_2S_2O_3$, dried over Na_2SO_4, and evaporated in vacuo. The crude product was purified by preparative TLC to give the iodocarbamate.

Phenylselenocarbamate Cyclization-----A mixture of the benzyl carbamate (0.2 mmol) and phenylselenyl chloride (0.23 mmol) in dichloroethane (1 ml) was refluxed under argon for 15 h. Most of the solvent was removed in vacuo and the residue was purified by preparative TLC without work-up to give the phenylselenocarbamate.

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9) When the benzyl carbamate (6) was allowed to react with phenylselenyl chloride in methylene chloride at room temperature, the corresponding adduct of phenylselenyl chloride to the double bond was obtained as a mixture of regioisomers in a 72% yield along with a 22% yield of the cyclized product (11b). The adduct could be converted to (11b) by refluxing in dichloroethane in a 96% yield.

10) All new compounds isolated in this work gave satisfactory spectral (IR, NMR, MS) and analytical (high resolution MS) data.

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