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Biscarbamoyl Diselenide as a Carbamoylating Reagent. A Convenient Method for the Preparation of ω-Haloalkyl Carbamates from Cyclic Ethers

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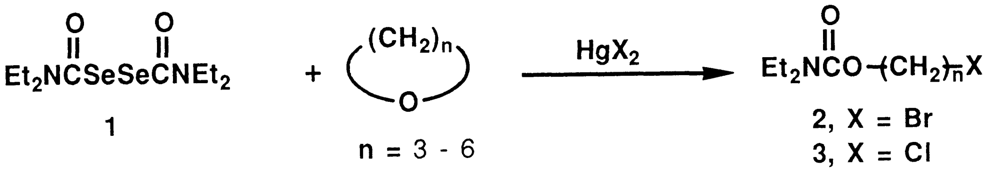
Treatment of 4- to 7-membered cyclic ethers with bis(N,N-diethylcarbamoyl) diselenide and mercury(II) halides resulted in halo-carbamoylative ring opening to give corresponding ω-haloalkyl carbamates in moderate to high yields.

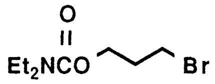
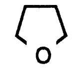
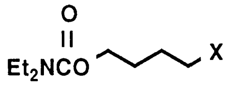
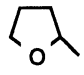
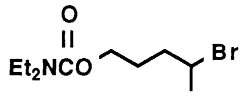
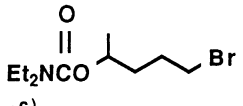
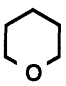
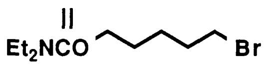
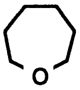
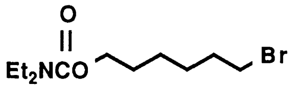
During the course of our study on the reactivity of biscarbamoyl diselenides,1) which can be easily prepared from amines, carbon monoxide and selenium,2) we have found that cyclic ethers undergo halo-carbamoylative ring opening with bis(N,N-diethylcarbamoyl) diselenide **1** in the presence of mercury(II) halides to give corresponding ω-haloalkyl carbamates **2** or **3** in good yields (Eq. 1). Although some alkyl carbamates bearing halogen atom at 3- or more remote position have been prepared from diols,3) isocyanates,4) and tetrahydrofuran,5) these methods involve considerable limitations of substrates and/or reagents. The reaction described herein will provide a convenient method for the synthesis of ω-haloalkyl carbamates.



(1)

For example, a mixture of **1**(1 mmol), $HgBr_2$(2 mmol), and tetrahydrofuran(THF) (6 mmol) in benzene(8 mL) was refluxed for 3 h. Extractive workup followed by column chromatography(SiO_2, benzene/ether(1:1)) afforded 1.66 mmol of 4-bromobutyl N,N-diethylcarbamate (**2b**)6) (0.417 g, 83%). In this reaction both of carbamoyl groups of **1** were efficiently utilized. Several representative results obtained by using 4- to 7-membered cyclic ethers are listed in Table 1. Oxetane gave 3-bromopropyl carbamate **2a**7) in 85% yield. Tetrahydropyran and oxepan were also converted to 5-bromopentyl and 6-bromohexyl carbamates **2d** and **2e**, respectively, in moderate yields.7) When $HgCl_2$ was employed, the reaction of THF was quite slow and gave the desired 4-chlorobutyl carbamate **3b**6) in poor yield, but the yield was improved by using THF as the solvent. The reaction of 2-methyltetrahydrofuran resulted in the formation of a mixture of 4-bromopentyl and 5-bromo-2-pentyl carbamates **2c** and **2c'** (85%; **2c**/**2c'** = 86/14).8) In the cases of epoxides such as

Table 1. Synthesis of Haloalkyl Carbamates

Entry	Cyclic ether	Product	Yield/%a)
1		 (2a)	85
2		 (2b), X = Br	83
3		(3b), X = Cl	77b)
4		 (2c)  (2c') (86 : 14)c)	85
5		 (2d)	44
6		 (2e)	51

Conditions: **1**(1 mmol), cyclic ether(6 mmol), HgBr$_2$(2 mmol), benzene(8 mL), reflux, 3 h. a) Isolated yields based on carbamoyl groups of **1**. b) HgCl$_2$(2 mmol) and THF(8 mL; as the solvent) were used. c) Determined by GLC.

propylene oxide, the products were often contaminated with alkenyl carbamates which were probably formed, sometimes as the major product, via dehydrobromination of the desired 2-bromoalkyl carbamates.

The activity of metal halides for the present reaction decreased in the order: HgBr$_2$ > CuBr$_2$ > HgCl$_2$ ~ SnCl$_4$. Other metal halides examined (AlCl$_3$, FeCl$_3$, and ZnCl$_2$) were ineffective.

Further investigation is now underway on the mechanism and synthetic application of this reaction.

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References

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6) Spectroscopic data were in good accord with those reported, see ref 5.
7) **2a**: oil; IR(neat) 1710 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 1.12(t, 6H, J=7.0), 2.19(quin, 2H, J=6.4), 3.18-3.36(m, 4H), 3.48(t, 2H, J=6.4), 4.21(t, 2H, J=6.4); MS(m/z) 238(M$^+$).
2d: oil; IR(neat) 1690 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 1.12(t, 6H, J=7.2), 1.46-1.60(m, 2H), 1.60-1.73(m, 2H), 1.82-1.94 (m, 2H), 3.18-3.34(m, 4H), 3.42(t, 2H, J=6.7), 4.08(t, 2H, J=6.4); MS(m/z) 267(M$^+$).
2e: oil; IR(neat) 1705 cm^{-1}; ^{1}H NMR(CDCl$_3$) δ 1.12(t, 6H, J=7.2), 1.33-1.55(m, 4H), 1.58-1.73(m, 2H), 1.81-1.94(m, 2H), 3.18-3.36(m, 4H), 3.41(t, 2H, J=6.9), 4.07(t, 2H, J=6.6); MS(m/z) 281(M$^+$).
8) The structural assignments of products **2c** and **2c'** were made by NMR spectra.

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