HETEROCYCLES, Vol. 31, No. 5, 1990

THE C-O BOND CLEAVAGE OF CYCLIC ETHERS WITH TRIS(PHENYLSELENO)-BORANE-LEWIS ACID

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Abstract-Tris(phenylseleno)borane (1) has a hard boron element and a soft selenium element, and therefore it was expected that 1 cleaves the C-O bond. Tetrahydrofuran and tetrahydropyran were cleaved with 1 in the presence of zinc iodide to produce the δ- and ε-phenylseleno alcohols (7 and 8). The C(5)-O bond of 2-methyltetrahydrofuran (5) was regioselectively cleaved with 1 and a catalytic amount of tin(IV) chloride to afford the δ-phenylseleno alcohol (12). The selenoborane (1) was a weak reagent for the C-O bond-cleavage and cleaved only cyclic ethers selectively.

A number of methods for the cleavage of ethers were recently developed.[1] Node et al. reported that the hard acid and soft nucleophile system is very effective in cleaving an ethereal carbon-oxygen bond.[2] On the other hand, tris(phenylseleno)borane (1)[3] is widely used for selenoacetalization of aldehydes or ketones,[4] and for ring-opening of epoxides.[5] This reagent consists of a hard element, boron and a soft element, selenium and therefore, we expected that the ethereal bond could be cleaved by the reagent.

Very recently, Miyoshi et al. reported that phenyl trimethylsilyl selenide-zinc iodide opened tetrahydrofuran rings to give trimethylsilyl ethers of δ-phenylseleno alcohols.[6] Here we describe the ring-opening reactions of tetrahydrofurans and tetrahydropyrans with selenoborane (1) and a catalytic amount of Lewis acid.

Selenoborane (1) reacted with tetrahydrofuran in the presence of a catalytic amount of anhydrous zinc iodide to give δ-phenylselenobutan-1-ol (7) quantitatively, but in the absence of zinc iodide to give 7 in only 4% yield. Anhydrous zinc iodide was effective in the case of 1, whereas moist zinc iodide was effective in the case of phenyl trimethylsilyl selenide.[6] Reaction of tetrahydropyran similarly *afforded an ε-phenylseleno alcohol (8) in 84% yield.* Although the reaction should proceed in principle with 1/3 molar amount of 1, the product (8) was given in 48% yield by use of 0.5 molar amount of 1 (Entry 3 in Table I). One molar amount of 1 was necessary for effecting the reactions sufficiently. Isochroman (4) underwent the bond cleavage between the benzylic carbon atom and the oxygen atom to give 2-(o-phenylselenomethyl)phenylethanol (9). When trifluoroacetic acid was used as a catalyst, 2-(o-tolyl)ethanol (10) was obtained in 18% yield in addition to seleno alcohol (9) (25%).

Next, we examined the regioselectivity of this reaction using 2-methyltetrahydrofuran (5). Reaction of 5 under the conditions described above proceeded with low regioselectivity to give 4-(phenylseleno)pentan-1-ol (11) and 5-(phenylseleno)-*pentan-2-ol (12) in 58% and 42% yields, respectively.* Since the molar ratio of the products (11/12) was not significantly changed, we searched for other Lewis acids. Reaction with zinc chloride caused the ring-opening in high yield without any regioselection (Entry 14). The bond cleavage reaction was not effectively catalyzed by titanium(IV) chloride, aluminum chloride, or boron trifluoride etherate. The product (12) was regioselectively provided using 0.03 molar amount of tin(IV) chloride (Entry 13). Reaction of dihydropyran (6) with zinc iodide afforded selenoacetal alcohol (13) in 93% yield through addition of selenoborane (1) to the double bond and successive ethereal bond cleavage, accompanied by selenoacetal selenide (14) in 7% yield.

Attempts to cleave the carbon-oxygen bonds of dialkyl ethers, alkyl aryl ethers, *diaryl ether, and lactones were unsuccessful.*

In summary, tris(phenylseleno)borane is a weak reagent for the carbon-oxygen bond fission and can be utilized for preparation of δ- and ε-phenylseleno alcohols by ring-opening of the tetrahydrofuran and tetrahydropyran derivatives.

Table 1 Reactions of Cyclic Ethers (2-6) with Tris(phenylseleno)borane (1)

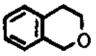
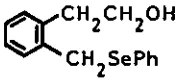
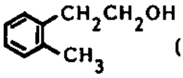
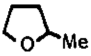
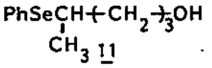
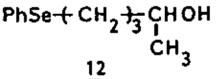
Entry No.	Ethers	$B(SePh)_3$ 1 Molar Ratio (Reaction Time)	Lewis Acids (Molar Ratio)	Products (% Yields)
1	 2	1.2 (3 d)	ZnI_2 (0.02)	$PhSe(CH_2)_4OH$ (100) 7
2	2	1.2 (3 d)	-	7 (4)
3	 3	0.5 (3 d)	ZnI_2 (0.02)	$PhSe(CH_2)_5OH$ (42) 8
4	3	1.2 (3 d)	ZnI_2 (0.02)	8 (84)
5	 4	1.2 (3 d)	-	 (trace) 9
6	4	1.2 (3 d)	ZnI_2 (3)	9 (94)
7	4	1.2 (3 d)	ZnI_2 (0.02)	9 (70)
8	4	1.2 (3 d)	CF_3CO_2H (0.1)	9 (25),  (18) 10
9	 5	1.2 (3 d)	ZnI_2 (0.02)	 $PhSe\underset{CH_3}{CH}(CH_2)_3OH$ (58) 11  $PhSe(CH_2)_3\underset{CH_3}{CH}OH$ (42) 12
10	5	1.2 (3 d)	ZnI_2 (1)	11:12/1:1.4 (75)
11	5	1.2 (3 d)	$SnCl_4$ (0.1)	11:12/1:11 (74)
12	5	1.2 (3 d)	$SnCl_4$ (0.2)	11:12/1:4 (71)
13	5	1.2 (3 d)	$SnCl_4$ (0.03)	11:12/1:20 (71)
14	5	1.2 (3 d)	$ZnCl_2$ (0.1)	11:12/1:1 (88)
15	 6	1.2 (79 h)	ZnI_2 (0.02)	$(PhSe)_2CH(CH_2)_4OH$ (93) 13 $(PhSe)_2CH(CH_2)_4SePh$ (7) 14

Table II Spectral Data of Products (7-14)

Products[*1]	^{1}H Nmr Spectral Data (60 MHz)($CDCl_3$) :(ppm)
7	1.50-2.25 (m, 4H), 2.55 (s, 1H), 2.90 (t, J=6 Hz, 2H), 3.55 (t, J=6 Hz, 2H), 7.13-7.55 (m, 5H).
8	1.23-1.95 (m, 6H), 2.60 (s, 1H), 2.88 (t, J=6 Hz, 2H), 3.55 (t, J=6 Hz, 2H), 7.13-7.58 (m, 5H).
9[*2]	2.00 (br s, 1H), 2.88 (t, J=6 Hz, 2H), 3.80 (t, J=6 Hz, 2H), 4.10 (s, 2H), 7.00-7.53 (m, 5H).
10[*2]	2.25 (s, 3H), 2.68-3.00 (m, 2H), 3.60-3.88 (m, 2H), 4.10 (s, 1H), 7.00-7.50 (m, 4H).
11[*3]	1.40 (d, J=7 Hz, 3H), 1.44-1.92 (m, 4H), 3.18-3.32 (m, 1H), 3.61 (t, J=6 Hz, 2H), 4.95 (br s, 1H), 7.20-7.26 (m, 3H), 7.45-7.54 (m, 2H).
12[*3]	1.14 (d, J=6 Hz, 3H), 1.49-1.57 (m, 2H), 1.66-1.87 (m, 2H), 2.11 (br s, 1H), 2.90 (t, J=7 Hz, 2H), 3.75 (m, 1H), 7.20-7.27 (m, 3H), 7.45-7.55 (m, 2H).
13	1.49-1.73 (m, 4H), 1.97-2.05 (m, 2H), 2.99 (s, 1H), 3.56 (t, J=6 Hz, 2H), 4.75 (t, J=7 Hz, 1H), 7.27-7.33 (m, 3H), 7.51-7.66 (m, 2H).
14	1.57-1.88 (m, 6H), 2.80 (t, J=7 Hz, 2H), 4.44 (t, J=6 Hz, 1H), 7.22-7.28 (m, 3H), 7.42-7.57 (m, 2H).

[*1] Molecular formulas of the products (7-14) were determined by the high resolution mass spectrometry.

[*2] The compounds (9 and 10) could not be separated and the methylene signals of (9 and 10) were overlapped in nmr spectrum.

[*3] The compounds (11 and 12) could not be separated and the product ratio was determined by the intensities of their methyl groups in nmr spectrum.

EXPERIMENTAL

Reaction of Tetrahydrofurans and Tetrahydropyrans with Tris(phenylseleno)borane in the Presence of Lewis Acid; General Procedure.

An ether compoud (1.0 mmol) was added to a stirred solution of tris(phenylseleno)borane (1) (1.2 mmol) and a Lewis acid (0.02 mmol) in dry dichloromethane (1 ml) under the reaction conditions described in Table I. The reaction mixture was poured into water and extracted with dichloromethane. The extracts were washed with brine, dried ($MgSO_4$), concentrated and purified by preparative tlc on silica gel using ethyl acetate-hexane (1:5). Products and yields are summarized in Table I and spectral data of the products are listed in Table II.

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Received, 26th February, 1990