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A Convenient Method for the Preparation of Ethers from Epoxides. Trityl Hexafluoroantimonate-Catalyzed Sequential Reactions, Rearrangement and Reductive Condensation, of Epoxides

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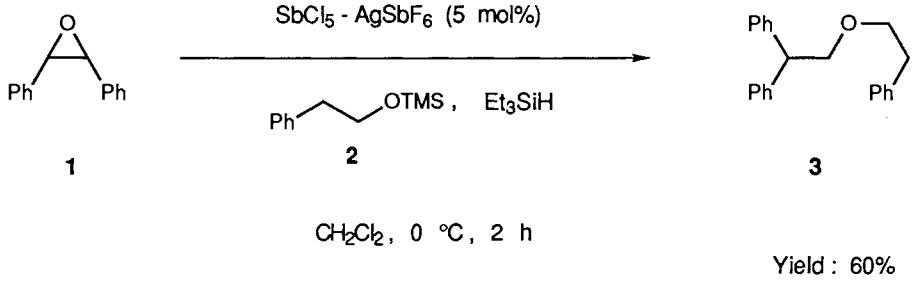
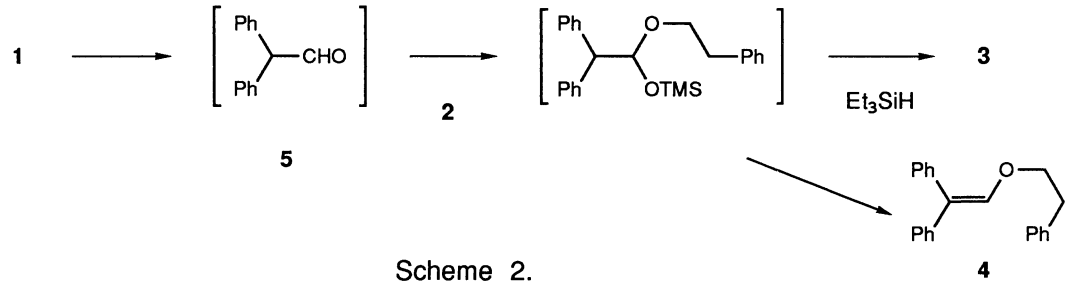
In the presence of a catalytic amount of trityl hexafluoroantimonate, sequential reactions, rearrangement and reductive condensation, of epoxides proceed smoothly to give the corresponding ethers in fairly good yields. Trityl hexafluoroantimonate (5 mol%) efficiently accelerates the above two sequential reactions.

In the previous papers,[1] we have reported that, in the presence of catalytic amounts of metal halides and silver salts, several synthetic reactions such as esterification, glycosylation, the Friedel-Crafts acylation, the Beckmann rearrangement, and pinacol rearrangement proceed smoothly to give the corresponding products stereoselectively in good yields. In order to expand the synthetic utility of these catalyst systems, a new sequential reactions of epoxides, versatile intermediates in organic synthesis,[2] were studied. We would like to report herein one-pot synthesis of ethers involving rearrangement[3] of epoxides, followed by reductive condensation reaction[4] with alkoxysilanes and triethylsilane using a catalytic amount of the catalyst system.

In the first place, the one-pot reaction of *cis*-2,3-diphenyloxirane (**1**) and trimethyl-(2-phenylethoxy)silane (**2**) was tried in the presence of a catalytic amount of antimony(V) salt, easily prepared in situ from $SbCl_5$ and $AgSbF_6$, which was effective in the catalytic Beckmann rearrangement[1d,e] and pinacol rearrangement.[1f] The sequential reactions proceeded smoothly to afford 2,2-diphenylethyl 2-phenylethyl ether (**3**) in 60% yield (Scheme 1). The pathway of this method is postulated as shown in Scheme 2. The catalyst is considered to promote two reactions; the rearrangement of epoxide and reductive condensation of diphenylacetaldehyde (**5**) with **2** and triethylsilane.



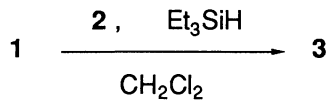
Scheme 1.



Scheme 2.

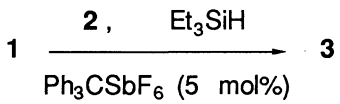
Next, in order to optimize the reaction conditions, several Lewis acids and solvents were examined by taking the above mentioned reaction of **1** as a model. The best acceleration of sequential reactions was achieved when the reaction was carried out in CH_2Cl_2 in the presence of trityl hexafluoroantimonate (Table 1,2).[5,6]

Table 1. Effect of Catalyst



Entry	Catalyst (5 mol%)	Yield/ %
1	$SbCl_5$ - $AgSbF_6$	60
2	$SbCl_5$ - $AgClO_4$	39
3	Ph_3CSbF_6	87[a)]
4	Ph_3CClO_4	47[a)]
5	TMSOTf	trace[a)]
6	BF_3•OEt_2	—

Table 2. Effect of Solvent

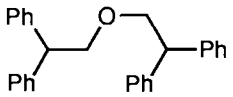
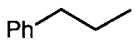
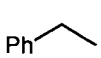
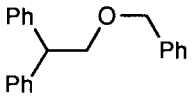
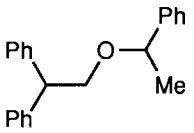
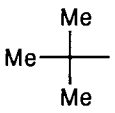
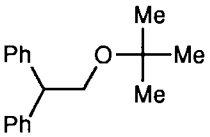
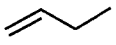
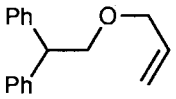
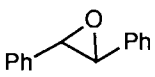
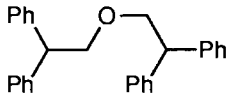
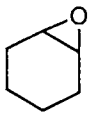
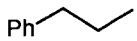
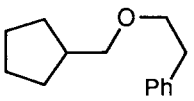
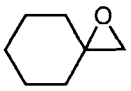
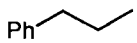
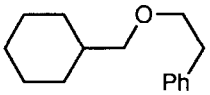
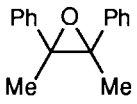
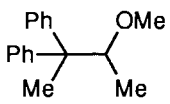
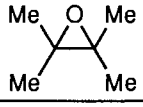
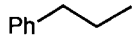
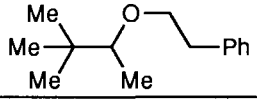


Entry	Solvent	Yield/ %
1	CH_2Cl_2	87
2	toluene	65
3	CH_3CN	—
4	ether	—

a) 2,2-Diphenylethenyl 2-phenylethyl ether (**4**) was also produced (2% (Entry 3), 33% (Entry 4), 43% (Entry 5)) (Scheme 2).

Several examples of the present reaction are demonstrated in Table 3. Regardless of the type of the migrating group (phenyl group (Entries 1,2,5), alkyl group (Entries 3,6), or hydrogen atom (Entry 4)), the reaction proceeds smoothly to give the corresponding products in good yields. Primary, secondary, and tertiary alkoxytrimethylsilanes are successfully employed in the present reaction. Among the reactions using the above silanes, benzyloxytrimethylsilane, *t*-butyloxytrimethylsilane, or allyloxytrimethylsilane provides a convenient method for the preparation of alcohols having synthetically useful protecting groups (Entry 1). Since epoxide is a starting material of this new sequential method, the preparation of ethers even when the corresponding carbonyl compounds are unstable is successfully accomplished.

Table 3. One-pot Synthesis of Ethers from Epoxides[a)]

Entry	Substrate	R (ROTMS)	Product	Temperature/ °C	Time/ h	Yield/%
1	**1**	—		0	2	85
	1		**3**	0	2	87
	1			0	2	83
	1			0	3	65
	1			0	3	65
	1			0	2	89
2		—		0	2	84
3[b)]				15 - 20	2	73
4				0	2	85
5[c)]		Me		15 - 20	overnight	88
6				0	2	74

a) Catalyst: Ph_3CSbF_6 (5 mol%).
b) The reaction was carried out in 1,4-dioxane. After addition of the epoxide and **2** to a solution of the catalyst, Et_3SiH was added.
c) MeOTMS was used 3 times molar quantity of the epoxide.

A typical experimental procedure for the reaction of *cis*-2,3-diphenyloxirane (**1**) is as follows; a solution of *cis*-2,3-diphenyloxirane (**1**) (98.1 mg, 0.500 mmol) in CH_2Cl_2 (1.5 ml) was added to a solution of trityl hexafluoroantimonate (12.0 mg, 5.01 mol%) in CH_2Cl_2 (2.0 ml) at 0 ℃. After stirring for 1 h, a solution of trimethy-(2-phenylethoxy)silane (**2**) (116.6 mg, 0.5999 mmol) in CH_2Cl_2 (0.5 ml) was added, followed by addition of a solution of triethylsilane (64.0 mg, 0.550 mmol) in CH_2Cl_2 (0.5 ml). After stirring for 1 h, the reaction was quenched with phosphate buffer (pH 7). The organic layer was separated and dried over Na_2SO_4. The evaporation of the solvent gave a crude product which was purified by preparative TLC to afford 131.0 mg (87%) of 2,2-diphenylethyl 2-phenylethyl ether (**3**).[7)]

References

1) a) T. Mukaiyama, I. Shiina, and M. Miyashita, *Chem. Lett.*, **1992**, 625; b) T. Mukaiyama, M. Katsurada, and T. Takashima, *ibid.*, **1991**, 985; c) T. Mukaiyama, K. Suzuki, J. S. Han, and S. Kobayashi, *ibid.*, **1992**, 435; d) T. Mukaiyama and T. Harada, *ibid.*, **1991**, 1653; e) T. Harada, T. Ohno, S. Kobayashi, and T. Mukaiyama, *Synthesis*, **1991**, 1216; f) T. Harada and T. Mukaiyama, *Chem. Lett.*, **1992**, 81.

2) J. Smith, *Synthesis*, **1984**, 629.

3) Only a few reagents are known as effective catalysts for this purpose. For example; D. Milstein and O. Buchman, *Tetrahedron Lett.*, **26**, 2257 (1974); K. Maruoka, S. Nagahara, T. Ooi, and H.Yamamoto, *ibid.*, **30**, 5607 (1989); K. Suzuki, M. Miyazawa, and G. Tsuchihashi, *ibid.*, **28**, 3515 (1987).

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5) The preparative method of various ethers from carbonyl compounds in the presence of a catalytic amount of trityl perchlorate was already reported from our laboratory.[4a)] In the present method, a better result was obtained by using trityl hexafluoroantimonate as a catalyst instead of trityl perchlorate (Table 1), and like trityl perchlorate, trityl hexafluoroantimonate was also a good catalyst of the reductive condensation using carbonyl compounds as substrates.

6) We had already reported that various trityl salts are quite effective catalysts in synthetic reactions. T. Mukaiyama and S. Kobayashi, *Heterocycles*, **25**, 205 (1987); K. Homma, H. Takenoshita, and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **63**, 1898 (1990), and references cited therein.

7) Physical properties of **3** are as follows. IR(neat) 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.83 (2H, t, J=7.1 Hz), 3.67 (2H, t, J=7.1 Hz), 3.97 (2H, d, J=7.2 Hz), 4.27 (1H, t, J=7.2 Hz), 7.0-7.3 (15H, m); MS, *m/z* (rel intensity) 301(M^+-1; 17), 197(4), 181(75), 167(19), 105(base peak), 91(24), and 77(12). Found: C, 87.20; H, 7.37%. Calcd for $C_{22}H_{22}O$: C, 87.38; H, 7.33%.

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