A NOVEL REACTION FOR THE FUNCTIONALIZATION OF EPOXY RESINS: NEW REGIO- AND CHEMOSELECTIVE RING-OPENING OF EPOXIDES WITH ARYL SILVL ETHER CATALYZED BY CESIUM FLUORIDE

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<u>Summary</u>: By use of cesium fluoride as a catalyst, aryl or alkyl glycidyl ethers were ring-opened by aryl trimethylsilyl ether to produce O-protected aryloxyhydrins with a quantitative regioselectivity for the first time. Alkyl silyl ether was ineffective for this ring-opening.

By the regioselective ring-opening of epoxides with trimethylsilyl azide¹, silyl halides², silyl amides³, and silylated arylselenol⁴, various O-protected functionalized hydrins prospective as synthetic intermediates were obtained. The ring-opening of epoxides by silyl ethers, however, has not been reported until now. If the reaction of epoxides with silyl ethers takes place, monoethers of vicinal diols again bearing silyl ether functions could be obtained. Thus these reactions are attractive in view of formation of useful organic intermediates as well as functionalization of epoxy resins or new developments in polymerization.

We describe here a novel chemo- and regioselective ring-opening of epoxides with aryl silyl ethers catalyzed by cesium fluoride for the first time. Development of the reaction to the functionalization of epoxy resins is also described.

Ring-opening of glycidyl phenyl ether (1) with trimethylsilyl phengxide (2) was investigated by use of various catalysts. As shown in Table 1, zinc iodide, which was effective for the addition reaction of phenyl trimethyl selenide to epoxides⁴, gave only poly(glycidyl phenyl ether). By trimethylsilyl triflate, 1 disappeared in high conversion, whereas only a small amount of adduct (10 %) was obtained. Tetrabutylammonium fluoride, an effective reagent for the cleavage of silyl ether, was also insufficient. On the contrary 2 mol% of cesium fluoride was used as a catalyst in a closed system, an adduct (3) was obtained in quantitative yield estimated by ¹H NMR analysis (an isolated yield of 81.2 %) at 130 °C for 1 h. The adduct 3 was stable enough for purification by silica gel column.

Cesium fluoride was the most effective catalyst among the various inorganic fluoride salts. The selective ring-opening to produce the trimethyl silyl ether of secondary alcohol with α -phenoxy substituent was confirmed from the ¹³C and ¹H NMR analyses of **3**⁵ (Eq. 1).



Table 1 Reaction of Glycidyl Phenyl Ether 1 and Trimethylsilyl Phenoxide 2 with Various Catalysts

Catalyst, mol%	Solvent	Temp. (°C)	Time (h)	Yield (%, ¹ H NMR)
ZnI ₂ , 50	THF	50	3	0 (polyether)
Ti(O- <u>i</u> Pr) ₄ , 25	THF	reflux	5	0
Me ₃ SiOTf, 10	CH ₂ Cl ₂	reflux	24	10 (decomp.67)
Bu ₄ NF, 4	THF	r.t.	3.5	6 (decomp.92)
 CsF, 2		1 30	 1	100 (81.2*)
KF, 2	-	130	1	67
LiF, 2	-	130	1	6

*Isolated yield.

The adduct 3 was oxidized by Jones' reagent to produce 1,3-diphenoxyacetone (4) in 71.4 % yield. In this oxidation, other products as aldehydes or acids were not obtained, which further confirmed the selective ring-opening (Eq. 2)



On the other hand, when glycidyl ether 1 and an equivalent amount of sodium phenoxide was reacted and subsequently treated with trimethyl silyl chloride, oligomerization proceeded mainly and adduct 3 was scarcely obtained.

In addition, the reaction of benzyl trimethylsilyl ether and glycidyl ether 1 catalyzed by CsF under the same conditions gave no adducts.

For various epoxides, the CsF catalyzed ring-opening with silyl ether 2 was also carried out. In case of 1 and n-butyl glycidyl ether, adducts by selective ring-opening were obtained in high yields (Table 2). Whereas 1,2epoxyhexane gave no adduct, and epichlorohydrin gave an adduct only in poor yield. Thus the remarkable chemoselectivity was observed for the ring-opening of epoxides. This result suggests that the epoxides enabled to be activated through the coordination to cesium cation are susceptible for ring-opening. High regioselectivity in the ring-opening might be attributed to the selective attack of the phenoxide anion to the less substituted and sterically favorable carbon on the epoxide activated by the coordination to metal cation. Then, the following scheme is proposed for the highly regio- and chemoselective ringopening of glycidyl derivatives with 2 catalyzed by CsF (Scheme 1).



Table 2 CsF Catalyzed Ring-opening of Various Epoxides with Silyl Ether 21)

¹)Reaction condition: CsF, 2 mol%, 130 °C, 1 h, closed, ²)Estimated by ¹H NMR analysis, ³)conversion, 30 % of monosilyl ether and 30 % of disilyl ether were isolated.





Activation of glycidyl ethers by the cesium ion was further ascertained by the selective ring-opening reaction of epoxides with phenol in the presence of CsF catalyst. The reaction of phenol with glycidyl ether 1 in the presence of 2 mol% of CsF at 130 °C for 1 h gave 1,3-diphenoxyisopropanol (5) in quantitative yield. However no reaction occurred for 1,2-epoxyhexane under the same reaction conditions. High selectivity was explained in this case also by the reaction of glycidyl ether activated through coordination to cesium ion with the phenoxide ion generated in situ by the equilibrium reaction of phenol and CsF (eq. 3).

Pho + PhOH
$$\xrightarrow{\text{CsF} (2 \text{ mol} \$)}$$
 Pho OPh (3)
1 5

When two equivalents of ether 1 was reacted with silyl ether 2, ringopening of 1 remained to be 58 %, which indicated that the ring-opening stopped at first step and the resulting adduct, alkyl silyl ether, did not react any more with the remaining epoxide.

As an application of this selective ring-opening reaction, we tried to synthesize a new type of epoxy resin with the silyloxy group. The CsF catalyzed reaction of a bifunctional aryl silyl ether (6) with two equivalents of bifunctional aryl glycidyl ether (7) gave an epoxy resin with a silyloxy group (8) in the conversion of aryl silyl group of 93 %, that was well correlated with the conversion of the epoxide group (50 %), estimated by ¹H NMR analysis.



On the other hand, the reaction of bifunctional aryl silyl ether 6 with two equivalents of 1,4-butanediol diglycidyl ether (9) gave the gel polymer in which the epoxide group disappeared completely. This result indicated that the ring-opening did not stop at the first step but proceeded successively to consume all epoxides. In the case of alkyl glycidyl ether 9 the epoxide group is presumed to be activated by CsF much extensively than aryl glycidyl ethers due to the higher coordinating function. Very interestingly this suggests the polymerizability of alkyl glycidyl ethers with a new catalyst system.

In conclusion we could find the selective ring-opening of glycidyl ethers with aryl trimethylsilyl ethers catalyzed by CsF. By applying this ring-opening reaction, functionalization of epoxy resins with a silyloxy group with new catalyst systems were successfully proceeded. Further studies in the functionalization and polymerization of various epoxides are in progress.

References and Notes

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- 5 Adduct 3: bp 150-160 °C/0.45 mmHg (Kugelrohr); ¹H NMR (CCl₄) δ: 0.15 (s, 9H), 3.90 (m, 4 H, PhOCH₂), 4.30 (m, 1 H, OCH<), 6.7 7.4 (m, 10 H, Ph); ¹³C NMR (CDCl₃) δ: 0.00 (SiMe₃), 69.16 (PhO<u>C</u>H₂), 69.55 (OCH<), 114.19, 120.57, 129.15, 158.34 (Ph). The abnormal adduct (silyl ether of primary alcohol) was not detected by NMR and GC analyses.</p>

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