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Lanthanoid-Catalyzed Ring-Opening Reaction of Epoxides with Acyl Halides

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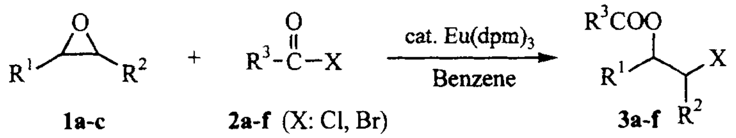
Abstract: Eu(dpm)$_3$ [dpm: dipivaloylmethanate] catalyzes the ring-opening reaction of epoxides with acyl halides affording the corresponding 2-haloalkyl esters. The stereochemical course was confirmed as *trans*-addition in the case of the reaction of cyclohexene oxide. © 1998 Elsevier Science Ltd. All rights reserved.

Transformation of epoxides to 1,2-disubstituted alkanes is one of the important processes in organic syntheses, and extensive studies on the regio- and stereochemistry of the ring-opening reaction of epoxides with several nucleophiles giving the 2-substituted alkanols catalyzed by transition metals, particularly lanthanoid metals, have been reported.[1] In continuing studies[2], we discovered that the lanthanoid(III) tris(dipivaloylmethanate) catalyzes the ring-opening reaction of epoxides with acyl halides to afford the corresponding 2-haloalkyl esters. To our knowledge, although a similar ring opening reaction of tetrahydrofuran (THF) with acyl halides promoted by Sm^{3+} was reported by Kagan,[3] this unique reaction is undoubtedly interesting as a first example of the ring opening reaction of epoxides. This communication describes an efficient and a stereoselective synthesis of 2-haloalkyl esters from the reaction of epoxides and acyl halides catalyzed by a lanthanoid complex (Eq 1).



1a-c **2a-f** (X: Cl, Br) **3a-f** (1)

At first, we examined the reaction of cyclohexene oxide (**1a**) (0.5 mmol) with benzoyl chloride (**2a**) (0.5 mmol) in benzene (1.5 mL) using a catalytic amount of various lanthanoid complexes (0.025 mmol) at 40°C for 2 h. The reaction proceeds smoothly to give *trans*-2-chlorocyclohexyl benzoate (**3a**) in 38% yield as a sole product. Although the reaction without catalyst gave no product, the reaction proceeded catalytically by the addition of lanthanoid complexes. Of the catalysts tested, 1,3-diketonato complexes of lanthanoid metals such as Ln(dpm)$_3$ are highly active for the reaction. The catalytic activity in this reaction with **1a** appears to be in the order Eu(dpm)$_3$ (38%) ~ Y(dpm)$_3$(37%) > Pr(dpm)$_3$ (18%) > Eu(pta)$_3$ (9%) > La(dpm)$_3$ (3%) ~ Eu(tfc)$_3$ (2%). The reaction using Eu(dpm)$_3$ catalyst was completed at 40°C for 24 h giving **3a** in 92% isolated yield. In additon, the product **3a** was also obtained in 84% yield at 80°C for 2 h

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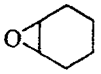
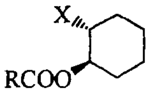
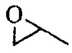
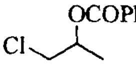
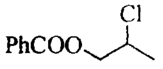
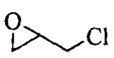
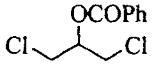
Table 1. Ring-Opening Reaction of Epoxides with Various Acyl Halides [a]

Epoxide	Acyl Halide	Time (h)	Product	Yield(%) [b]
 **1a**	PhCOCl (**2a**)	24	 **3a**: R = Ph, X = Cl	92
	PhCOBr (**2b**)	15	**3b**: R = Ph, X = Br	91
	CH_3COCl (**2c**)	6	**3c**: R = CH_3, X = Cl	89
	n-C_3H_7COCl (**2d**)	4	**3d**: R = C_3H_7, X = Cl	86
	c-$C_6H_{11}COCl$ (**2e**)	3	**3e**: R = c-C_6H_{11}, X = Cl	90
	 COCl (**2f**)	24	**3f**: R = , X = Cl	85
 **1b**	**2a**	16	 **3g** +  **3h**	70 [c]
 **1c**	**2a**	16	 **3i**	79

a) Reaction conditions: epoxide (1.0 mmol), acyl halide (1.5 mmol), $Eu(dpm)_3$ (0.05 mmol), benzene (3.0 mL), 40°C. b) Isolated yield based on epoxide. c) Mixture of **3g** and **3h** (**3g** : **3h** = 73 : 27).

without any side-reaction.

The representative results for the reaction of various acyl halides with epoxides are shown in Table 1. The reaction of cyclohexene oxide (**1a**) with various acyl halides, gave the corresponding *trans*-2-halocyclohexyl esters in 86~92% yields. The reactivity of acyl halides toward **1a** appears to be in the order c-$C_6H_{11}COCl$ (**2e**) ~ n-C_3H_7COCl (**2d**) ~ CH_3COCl (**2c**) > PhCOBr (**2b**) > $CH_3CH{=}CHCOCl$ (**2f**) > PhCOCl (**2a**). The stereochemistry of the products **3a-f** was assigned as *trans*- configuration by the proton couplings at C_1 and C_2 position (J = 9.0 - 9.3 Hz). As expected, the reaction using monosubstituted epoxides such as propylene oxide (**1b**) afforded the mixture of two regioisomers, **3g** and **3h** (73:27). However the reaction of epichlorohydrin (**1c**) with benzoyl chloride (**2a**) gave the corresponding ester **3i** as a single product.

Further mechanistic study and synthetic application are now under investigation.

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