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REGIOSELECTIVE RING CLEAVAGE OF OXIRANES CATALYZED BY ORGANOTIN HALIDE - TRIPHENYLPHOSPHINE COMPLEX

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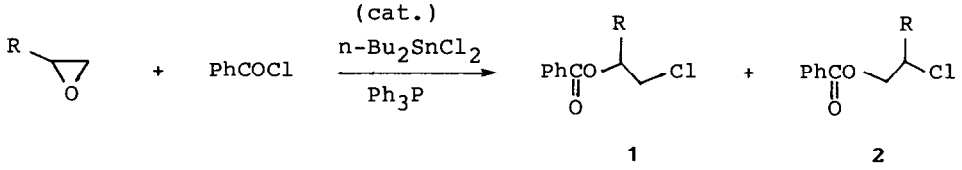
Abstract: Vicinal chloroesters are formed in high yield from the reaction of oxiranes and benzoyl chloride in the presence of organotin halide - triphenylphosphine complex with enhanced regioselectivity in oxirane ring cleavage.

Regioselective ring cleavage of oxiranes is a subject of current interest due to the wide application in organic synthesis.[1] Although a variety of reagents are useful, the exploration of new catalysts must be studied because of the general importance of this cleavage reaction. We have already reported that organotin halides, when complexed with Lewis bases, played as efficient catalysts for cycloaddition of heterocumulenes with oxiranes[2] or oxetanes.[3] In the course of these studies, we have found that this organotin halide complexes may be effective for regioselective ring cleavage of oxiranes to produce organotin β-haloalkoxides.[4,5]

Thus we report here that oxiranes react with benzoyl chloride easily to give vicinal chloroesters[6] in the presence of catalytic amounts of n-Bu_2SnCl_2 and Ph_3P. In addition, this method has several advantages in terms of neutral and mild reaction conditions, stability of the catalyst and high chemo- and regioselectivity.



1 2

A facile complex formation of organotin halides with Lewis bases is well known.[7] Although the structures and stabilities are intensively investigated, these complexes are hardly used in organic synthesis.[8]

The following procedure is representative. Oxirane (10 mmol) and benzoyl chloride (1.40 g, 10 mmol) were successively added to a stirred solution of Bu_2SnCl_2 (0.31g, 1 mmol) and Ph_3P (0.26 g, 1 mmol) in benzene (5

ml), the reaction mixture was stirred at 60°C. The formation of product was monitored by GLC analysis. After the reaction, the solutuion was concentrated under reduced pressure and the residue was chromatographed (Silica gel, eluted by benzene) to give vicinal chlorobenzoates. The regioselectivity was determined by ^{1}H-NMR spectra.

Table 1. Reaction of Methyl Oxirane with Benzoyl Chloride.[a]

Cat. System	Time (h)	Yield[b] (%)	Ratio[c] 1 : 2
Bu_2SnCl_2	24	13	46 : 54
Me_2SnCl_2	5	20	46 : 54
$SnCl_2$	5	55	43 : 57
Ph_3P	24	0	
Bu_2SnCl_2-Ph_3P	1	100	94 : 6

[a]Methyl oxirane 50 mmol, PhCOCl 10 mmol, catalyst 1 mmol, benzene 5 ml, temp. 60°C. [b]Based on PhCOCl and determined by GLC using an internal standard. [c]Determined by ^{1}H-NMR($CDCl_3$), for **1**: 1.45 (d,3H,CH_3), 3.65 (d,2H,CH_2Cl), 5.10-5.50 (m,1H,CH), 7.10-8.20 (m,5H,Ph); for **2**: 1.55(d,3H, CH_3), 4.10-4.50 (m,3H,CH_2Cl and CH), 7.10-8.20 (m,5H,Ph).

Table 1 shows the results of the reaction of methyl oxirane with benzoyl chloride. Organotin chlorides alone have low catalytic activities, and cleavages are not regiospecific. Triphenylphosphine has also no catalytic activity. On the contrary, the complexed catalyst, Bu_2SnCl_2-Ph_3P gave **1** quantitatively via regioselective cleavage at the less-substituted carbon (β-cleavage).

Moreover, as shown in Table 2, exclusive formations of **1** were achieved for the reactions of ethyl oxirane (entry 1), chloromethyl oxirane (entry 2), glycidyl ether (entry 3) and glycidyl ester (entry 4). Thus, the presence of certain functional group, such as ether, vinyl ester and halogen moieties can be tolerated in this reaction system. Generally, 2,2-dimethyl oxirane and phenyl oxirane favors α-cleavage because of the electronic effect.[9] In fact, only **2** was formed without bases (entry 6), however, the ratio of **1** was increased by the addition of bases (entries 7 and 8) in the reaction of phenyl oxirane. The tin complexes have a property to promote β-cleavage of oxiranes. Using cyclohexene oxide, the oxirane bridge was cleaved quite stereoselectively

Scheme 1

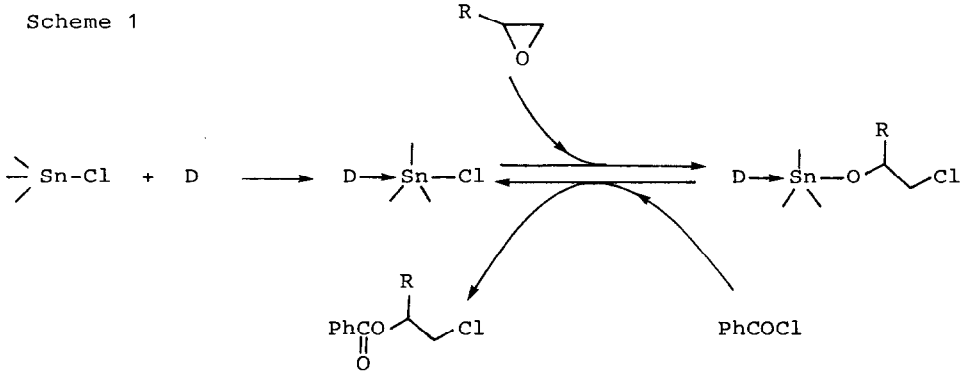
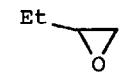
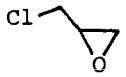
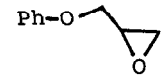
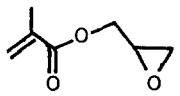
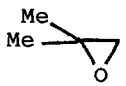
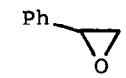
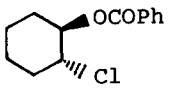


Table 2. Reaction of Oxiranes and Acid Chlorides.[a]

Entry	Oxirane	Cat. System	Time (h)	Yield[b] (%)	Ratio[c] 1 : 2
1		Bu_2SnCl_2-Ph_3P	1	100	94 : 6
2		"	1	100	100 : 0
3		"	1	100	100 : 0
4		"	1	100	100 : 0
5		"	6	56	43 : 57
6		Bu_2SnCl_2	24	63	0 :100
7		Bu_2SnCl_2-Ph_3P	4	90	33 : 67
8		Bu_3SnCl-DBU	24	98	45 : 55
9		Bu_2SnCl_2-Ph_3P	1	100	

[a]Reaction conditions: oxirane 10 mmol, PhCOCl 10 mmol, tin chloride 1 mmol, base 1 mmol, benzene 5 ml, temp. 60°C, [b]Determined by GLC using an internal standard. [c]Determined by ^{1}H-NMR.

leading only to trans-chloroester resulting from the usual anti-opening of the ring (entry 9).

The course of the overall reaction can be interpreted as follows. In the Bu_2SnCl_2 complex, the halogen is activated by the coordination of a Lewes base toward a tin atom, and the positive tin atom attack the oxirane

oxygen. This is followed by a nucleophilic attack by the halide ion which has been formed in situ at the less substituted carbon atom of the stannylated oxirane ring, and an organotin β-haloalkoxide is formed. The addition of benzoyl chloride finally accomplishes a rapid esterification, accompanied by the regeneration of the catalyst (Scheme 1).

In summary, the organotin halide - Lewis base complexes proved to be a highly practical and effective catalyst for chemo- and regioselective ring cleavage of oxiranes with acid chlorides. The scope and synthetic application of this method is under investigation.

References and Notes

1) See for example, C. H. Behrens and K. B. Sharpless, Aldrichimica Acta., **16**, 67 (1983); A. S. Rao, S. K. Paknikar and J. G. Kirtane, Tetrahedron, **39**, 2323 (1983); J. G. Smith, Synthesis, 629 (1984).
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4) Fiorenza et al. reported the ring cleavage promoted by Me_3SnX (X= halogen) to produce organotin β-haloalkoxides; M. Fiorenza, A. Ricci, M. Taddei and D. Tassi, Synthesis, 640 (1983).
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6) Oxiranes were reported to be cleaved by acetyl chlorides in the presence of chromyl chloride. However, satisfactory results were not obtained in its regioselectivity; J. E. Backwell, M. W. Young and K. B. Sharpless, Tetrahedron Lett., **40**, 3523 (1977).
7) See for example A. K. Sawer "Organotin Compounds Vol. 1"; Marcel Dekker: New York, 1971, p. 81 and references cited therein; Bu_2SnCl_2 is reported to form 1:1 complex with tertiary phosphine in benzene solution. Y. Farhangi and D. P. Graddon, J. Organomet. Chem., **87**, 67 (1975).
8) R. Nomura, M. Kimura, S. Teshima, A. Ninagawa and H. Matsuda, Bull. Chem. Soc. Jpn., **55**, 3200 (1982); A. Baba, H. Meishou and H. Matsuda, Makromol. Chem., Rapid Commun., **5**, 665 (1984).
9) R. E. Parker and N. S. Isaacs, Chem. Rev., 737 (1959).

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