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YTTRIUM COMPOUNDS: NEW CATALYSTS FOR THE REGIOSELECTIVE ACYLATIVE CLEAVAGE OF EPOXIDES

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Abstract: The use of Cp_2YCl and YCl_3 as effective catalysts for the regioselective acylative cleavage of epoxides, especially for the conversion of α,β-epoxyketones to α-chloroenones is described.

The application of rare earth reagents in organic synthesis has been growing fast since the late seventies[1]. In the course of our study on the cleavage reaction of the Cp-Y π bond of Cp_2YCl with electrophilic reagents, we found that fulvenes were obtained in high yield when aldehydes or ketones were used as the

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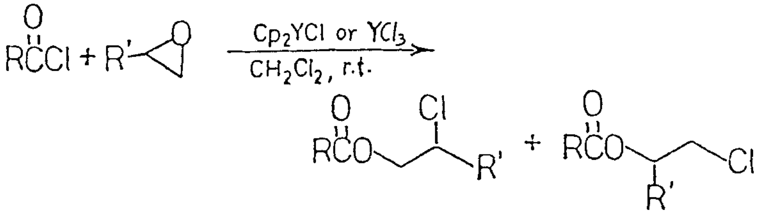
electrophilic reagents[2]. However, in the case of acyl chlorides, which are more reactive electrophilic reagents than aldehydes and ketones, 4-chlorobutyl esters as well as diacylcyclopentadienes were isolated, suggesting that Cp_2YCl might be a good catalyst for the acylative ring-opening of tetrahydrofuran[3]. Further studies have shown that Cp_2YCl and $LnCl_3$ did function as efficient catalysts for this cleavage reaction in dichloromethane[4]. Naturally, we would explore the application of these Lewis acidic rare earth compounds as catalyst to the acylative cleavage of other types of cyclic ethers. Ln-catalyzed epoxide ring cleavage has been reported, however,the only examples are those with nucleophiles such as RSH[5] and Me_3SiCN[6], catalyzed by anhydrous lanthanide trichlorides. We here wish to report that Cp_2YCl and YCl_3 catalyze the regioselective acylative cleavage of epoxides with electrophilic reagents, namely acyl chlorides, under mild conditions.

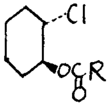
Epoxides reacted with acyl chlorides readily to give vicinal chloroesters in the presence of 1% (molar ratio) Cp_2YCl (eq. 1). The results are summarized in



(1)

Table 1. Phenyl oxirane favours α-cleavage, while alkyl oxiranes favour β-cleavage, with chloromethyl oxirane giving exclusive formation of **2**. Cyclohexene

Table 1. Cp_2YCl Catalyzed Acylative Cleavage of Epoxides

Entry	R	R′	Time(h)	Yield(%,1+2)*	1/2#
a	CH_3	C_6H_5	13	95	88/12
b	CH_3	$C_{14}H_{29}$	24	98	42/58
c	CH_3	CH_2Cl	24	98	0/100
d	C_6H_5	C_6H_5	20	93	75/25
e	C_6H_5	$C_{14}H_{29}$	24	97	14/86
f	C_6H_5	CH_2Cl	20	92	0/100
g	C_6H_5		24	97	
h	CH_3		24	95	

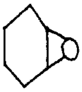
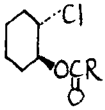
*. Isolated yield. #. Determined by ^1H NMR.

oxide was cleaved stereoselectively leading only to trans-chloroester.

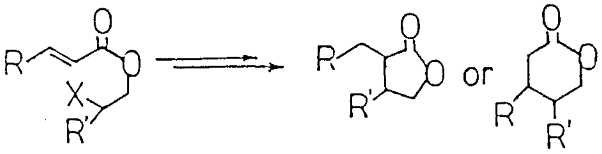
YCl_3 also catalyzed regioselective acylative cleavage of epoxides under mild conditions (eq. 1). Table 2 gives the results. However, YCl_3 was less efficient as catalyst when compared to Cp_2YCl. 10% YCl_3 was required to reach the activity of 1% Cp_2YCl. The two catalysts have similar regioselectivity, as shown in Table 1 and 2.

One of the methods for the synthesis of lactones is the intramolecular cyclisation of vicinal haloester (Scheme 1). Products obtained from the reaction of epoxides with cinnamoyl chloride (Table 2, Entry i, j, k) are starting materials for this cyclisation. Since vicinal iodoesters perform such a cyclisation more

Table 2. YCl_3 Catalyzed Acylative Cleavage of Epoxides

Entry	R	R′	Time(h)	Yield(%,1+2)*	1/2#
a	CH_3	C_6H_5	24	99	82/18
b	CH_3	$C_{14}H_{29}$	24	98	45/55
c	CH_3	CH_2Cl	24	97	0/100
d	C_6H_5	C_6H_5	24	97	100/0
e	C_6H_5	$C_{14}H_{29}$	24	97	17/83
f	C_6H_5	CH_2Cl	24	99	0/100
g	C_6H_5		24	98	
h	CH_3		24	88	
i	$C_6H_5CH{=}CH$	C_6H_5	20	98	78/22
j	$C_6H_5CH{=}CH$	$C_{14}H_{29}$	40	94	28/72
k	$C_6H_5CH{=}CH$	CH_2Cl	36	100	0/100

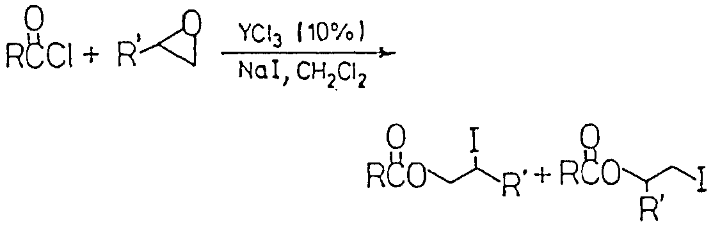
*. Isolated yield; #. Determined by ^1H NMR.



3

Scheme 1

easily, we explored the possibility of gaining access to vicinal iodoesters by the addition of NaI into the above reaction system. As expected, in some cases vicinal iodoesters were acquired in very high yield with excellent regioselectivity (eq. 2 and Table 3). Using acetyl chloride as electrophilic reagent, however,both vicinal iodoester and chloroester (about 1:3) were obtained. Addition of NaBr still afforded vicinal chloroester, no vicinal bromoester was detected by ^{1}H NMR.



(2)

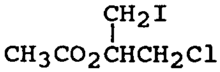
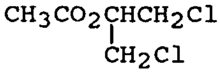
4 **5**

It was interesting to note that α,β-epoxycyclohexanone (**6**) reacted with benzoyl chloride in the presence of 10 mol% YCl_3 generating α-chloro-α,β-cyclohexenone (**7**) instead of resulting in usual acylative cleavage (eq. 3). Using **9** as substrate,the same observation was obtained (eq. 4), but for **11** and **14**, usual acylative cleavage products were afforded(eq. 5 and 6). Although the reason why this elimination occurs in some cases is now unclear, it worth noting that this reaction might provide a new convenient method for the synthesis of α-chloroenones.

Experimental

All the reactions were carried out under purified argon. CH_2Cl_2 was distilled from CaH_2 under argon. An-

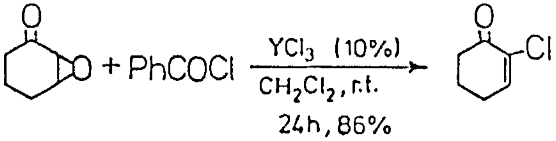
Table 3. YCl_3 Catalyzed Acylative Cleavage of Epoxides in the Presence of NaI

Entry	R	R′	Time(h)	Yield(%,4+5)[1]	4/5[2]
a[3]	C_6H_5	CH_2Cl	24	no reaction[2]	
b	C_6H_5	CH_2Cl	24	99	0/100
c	$C_6H_5CH{=}CH$	CH_2Cl	30	98	0/100
d	$C_6H_5CH{=}CH$	C_6H_5	17	92	100/0
e	CH_3	CH_2Cl	20	26	 $CH_3CO_2CH(CH_2I)CH_2Cl$
				71	 $CH_3CO_2CH(CH_2Cl)CH_2Cl$
f[4]	C_6H_5	CH_2Cl	24	no brominated ester[2]	

1. Isolated yield; 2. Determined by ^1H NMR;
3. no YCl_3 was used; 4. NaBr was in place of NaI.

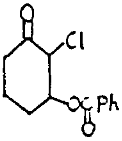
hydrous YCl_3[7] was used and Cp_2YCl was prepared according to the reported method[8]. Epoxides **6**, **9**, **11** and **14** were prepared by the modified method based on the literature[9], and the other ones were purchased from Tokyo Kasei. M.p.s were uncorrected. ^1H NMR spectra were recorded in CCl_4 or $CDCl_3$ on a Varian EM-360L (60 MHz) or AM-300 (300 MHz) spectrometer with $SiMe_4$ as the internal standard. IR spectra were recorded on a Shimadzu IR-440 instrument. MS data were obtained on a Finnigan 4021 spectrometer.

General Procedure for Table 1. Into a solution of Cp_2YCl(17.8 mg, 0.07 mmol) in 1 ml CH_2Cl_2, styrene oxide (840 mg, 7 mmol) and acetyl chloride (550 mg, 7 mmol)



(3)

6 7



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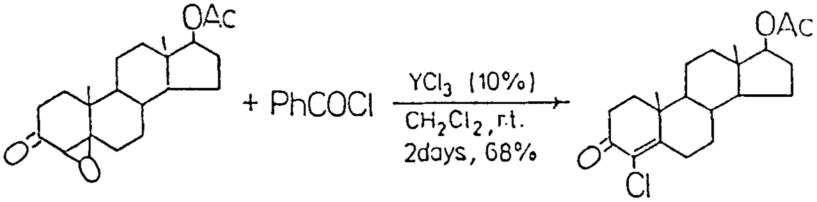
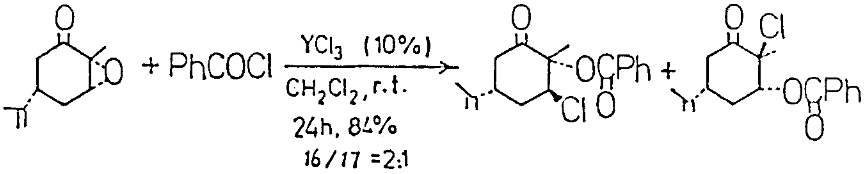


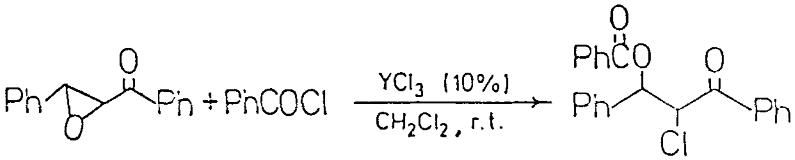
(4)

9 10



(5)

11 12 13



(6)

14 15

were added under argon. After the given time the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography to afford the mixture of **1** and **2**. Ratio of **1/2** was determined by ^{1}H NMR.

1a/2a[10]. ^{1}H NMR, δ: **1a**, 2.06(s, 3H), 4.45(d, J=7Hz, 2H), 5.11(t, J=7Hz, 1H), 7.33(s, 5H); **2a**, 2.10(s,3H), 3.36(d, J=7Hz, 2H), 6.63(t, J=7Hz, 1H), 7.33(s, 5H).

1b/2b[11]. ^{1}H NMR, δ: **1b**, 0.87(t,3H), 1.0-1.8(m,26H), 2.08(s, 3H), 4.0-4.3(m, 3H); **2b**, 0.87(t, 3H), 1.0-1.8 (m, 26H), 2.05(s, 3H), 3.60(d, J=6Hz,2H), 4.87(m, 1H).

2c[12]. ^{1}H NMR, δ: 2.05(s, 3H), 3.70(d, J=5Hz, 4H), 5.06(m, 1H).

1d/2d[13,14]. ^{1}H NMR, δ: **1d**, 4.45(d, J=7Hz, 2H), 4.96 (t, J=7Hz, 1H), 7.0-7.5(m, 8H), 7.89(m, 2H); **2d**, 3.70(d, J=6Hz,2H), 6.83(t, J=6Hz, 1H), 7.0-7.5(m, 8H), 8.05 (m, 2H).

1e/2e[11]. ^{1}H NMR, δ: 2e, 0.77(t, J=5Hz, 3H), 1.0-1.5 (m,26H), 4.1-4.4(m, 3H), 7.38(m, 3H), 7.95(m, 2H); **1e**, 0.77(t, J=5Hz, 3H), 1.0-1.5(m, 26H), 3.67(d, J=5Hz, 2H), 5.09(m, 1H), 7.38(m, 3H), 7.95(m, 2H).

2f[13,14]. ^{1}H NMR, δ: 3.72(d, J=5Hz, 4H), 5.20(m, 1H) 7.34(m, 3H), 7.92(m, 2H).

1g[13,14]. ^{1}H NMR, δ 1.50(m, 3H), 1.78(m, 3H), 2.25(m, 2H), 4.0(td, J=9Hz and 4Hz, 1H), 5.05(td, J=9Hz and 4Hz, 1H), 7.50(m, 3H), 8.09(m, 2H).

1h[10,15]. ^{1}H NMR, δ 1.50(m, 3H), 1.76(m, 3H), 2.03(s, 3H), 2.30(m, 2H), 3.90(td, J=9Hz and 4Hz, 1H), 5.02 (td, J=9Hz and 4Hz, 1H).

General procedure for Table 2 was as described above, but 10 mol% YCl_3 was used instead of 1 mol% Cp_2YCl, and the concentrations of reagents were 1.0 M.

Satisfactory spectral data were obtained for the products. The ratio of **1**/**2** was determined by ^{1}H NMR.

1i/**2i**. ^{1}H NMR, δ . **1i**, 4.37(d, J=7Hz, 2H), 4.98(t, J=7Hz, 1H), 6.20(d, J=17Hz, 1H), 7.52(d, J=17Hz, 1H), 7.24(m, 10H); **2i**, 3.23(d, J=7Hz, 2H), 6.55(t, J=7Hz), 6.20(d, J=17Hz, 1H), 7.52(d, J=17Hz,1H), 7.24(m, 10H). Anal. Calcd. for $C_{17}H_{15}ClO_2$: C, 71.21; H, 5.27. Found: C, 70.95; H, 5.50%.

1j/**2j**. ^{1}H NMR, δ . **1j**, 0.87(t, 3H), 1.10-2.0(m, 26 H), 3.63(d, J=5Hz, 2H), 5.10(m, 1H), 6.40(d, J=17Hz, 1 H), 7.70(d, J=17Hz, 1H), 7.41(s, 5H); **2j**, 0.87(t,3H), 1.10-2.0(m, 26H), 4.0-4.4(m, 3H), 6.40(d, J=17Hz, 1H), 7.70(d, J=17Hz, 1H), 7.41(s, 5H). Anal. Calcd. for $C_{25}H_{39}ClO_2$: C, 73.77; C, 9.66. Found: C, 74.01; H, 9.48%.

2k. ^{1}H NMR, δ 3.72(d, J=4Hz, 4H), 5.15(m,1H), 6.35 (d, J=17Hz, 1H), 7.65(d, J=17Hz, 1H), 7.34(s, 5H). m/z 258(M^+, 3.10), 222(11.75), 131(100). Anal. Calcd. for $C_{12}H_{12}Cl_2O_2$: C, 55.62; H, 4.67. Found: C, 55.84; H, 5.02%.

General Procedure for Table 3. Into a mixture of YCl_3 (19.6 mg, 0.1 mmol) and NaI (180 mg, 1.2 mmol) in CH_2Cl_2 (2 ml), chloromethyl oxirane (92.5 mg, 1 mmol) and benzoyl chloride (141 mg, 1 mmol) were added. The work-up procedure was as described above. Because of the readily deiodination of iodoesters, satisfactory elemental analytical data were not obtained for **5b**, **5c** and **4d**.

5b. ^{1}H NMR, δ 3.46(d,J=5Hz,2H), 3.77(d, J=4Hz, 2H), 5.00(m, 1H), 7.42(m, 3H), 8.00(m, 2H); m/z 325 (M^++H, 6.14), 197(73.34), 123(18.39), 105(100).

5c. ^{1}H NMR, δ 3.43(d, J=6Hz, 2H), 3.72(d,J=5Hz,2H), 4.90(m, 1H), 6.32(d, J=17Hz, 1H), 7.63(d, J=17Hz, 1H), 7.34(s, 5H).

4d. ^{1}H NMR, δ 4.62(d,J=8Hz,2H), 5.20(t, J=8Hz, 1H), 6.32(d, J=17Hz, 1H), 7.63(d, J=17, 1H), 7.37(m, 10H); m/z 251(46.66), 231(7.85), 149(9.99), 132(100).

The procedures for the reaction of α,β-epoxyketones were identical to the general procedure for Table II.

7. m.p. 71-72°C. ^{1}H NMR, δ 2.20(m,2H), 2.53(m,4H), 7.10(m, 1H); IR(KBr) 1685cm^{-1}; m/z 132(23.85), 130(M$^+$, 64.33); Anal. Calcd for C_6H_7ClO: C, 55.19; H, 5.40. Found: C, 55.32; H, 5.18%.

10. m.p. 219-220°C. ^{1}H NMR, δ 3.59(t, J=6Hz, 1H), 2.55(m, 2H), 2.03(s,3H), 1.24(s,3H), 1.0-2.17(m, 17H); IR(KBr) 1730, 1680cm^{-1}; m/z 366(4.42), 364(M$^+$,14.29), 328(100),322(23.54),287(37.68),268(57.67), 158(40.49), 147(58.18); Anal. Calcd for $C_{21}H_{29}ClO_3$: C, 69.12; H, 8.01. Found: C, 68.81; H, 7.66%.

12. oil. ^{1}H NMR, δ 1.33(s, 3H), 1.73(s, 3H), 1.75-2.0(m, 2H), 2.33(m, 1H), 2.53(m,1H), 2.67(m, 1H), 3.35 (s, 1H), 4.71(s, 1H), 4.76(s, 1H), 7.50(m,3H), 8.05(m, 2H); IR(neat), 1776, 1710, 1597cm^{-1}; m/z 306(M$^+$,0.18), 271(0.24), 165(3.69), 149(3.34), 105(100), 77(35.30); $[\alpha]^{D}_{15}$ =-88.2°(c=1.5, CHCl$_3$). Anal. Calcd. for $C_{17}H_{19}ClO_3$: C, 66.56; H, 6.24. Found: C, 66.74; H, 6.27%.

13. oil. ^{1}H NMR, δ 1.60(s, 3H), 1.79(s, 3H), 2.05-3.0(m, 5H), 4.86(s,2H), 5.66(s, 1H), 7.55(m, 3H), 8.03 (m, 2H); IR(neat) 1771, 1715, 1638cm^{-1}; m/z 307(M$^+$+H, 1.17), 271(0.32), 186(2.20), 184(6.57), 149(15.11),106 (100), 77(41.07). Anal. Cald for $C_{17}H_{19}ClO_3$: C, 66.56; H, 6.24. Found: C, 66.47; H, 6.24%.

15. m.p. 94-95°C. ^{1}H NMR δ 5.48(d, J=9Hz,1H), 6.60 (d, J=9Hz,1H), 7.48(m, 11H), 7.88(m, 2H), 8.17(m, 2H); IR(KBr) 1710,1680,1600,1594cm^{-1}; m/z 365(M$^+$+H, 0.10), 241(3.32), 224(7.06), 138(2.23), 106(100), 77(32.31); Anal. Calcd. for $C_{22}H_{17}ClO_3$: C, 72.43; H, 4.70. Found: C, 72.65; H, 4.76%.

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