COBALT CATALYSED REGIOSELECTIVE CLEAVAGE OF OXIRANES WITH ACYLCHLORIDES

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Abstract: Oxiranes can be cleaved in a regioselective manner with acylchlorides in presence of Cobalt(II) chloride to the corresponding vicinal chloroesters in high yields.

Regioselective cleavage of oxiranes with carbon and heteronucleophiles has gained prominence as an important synthetic transformation^{1, 2} in organic synthesis. In order to gain access to vicinal chlorobenzoates and chlorocrotonates which we required for free radical intramolecular cyclisation (Scheme), we explored the possibility of opening the oxiranes with the corresponding acylchlorides.



Shibata et al have recently shown that such transformations can be achieved by $n-Bu_2SnCl_2-PPh_3$ catalysed³ opening of oxiranes with benzoylchloride. Their reagent is quite efficient but has the disadvantage of being effective only at higher temperatures. Our continued interest in cobalt mediated acylations⁴ led us to explore the possibility of using cobalt complex for such a cleavage of oxiranes and a summarised account of these findings is given below.

Oxirane (10 m mol) and acid chloride (10 m mol) were successively added to a stirred solution of dry cobalt(II) chloride (50 mg) in dry acetonitrile at 0° C and the mixture was stirred at ambient temperature for 1 hr. Removal of acetonitrile under reduced pressure followed by usual work-up gave chloroesters (see table) in very high yields. A variety of oxiranes can be cleaved under very mild conditions to mainly one regioisomer as indicated by their crude NMR. In most cases the products were quite pure and did not require any chromatographic separation. Thus Co(II)Cl₂ mediated regioselective acylative cleavage of oxiranes presents an attractive route to synthetically important vicinal chlorobenzoates and chlorocrotonates.

Entry	Oxiranes	Acyl Chlorides	Product (s) ^{b,c}	Yield %
1	\sim	Ph Cl	$c_1 \stackrel{\text{Ph}}{\longrightarrow} \stackrel{\text{Ph}}{\longrightarrow} \stackrel{\text{Ph}}{\longrightarrow} c_1 $	78
2	\sim	°⊐ cı	$\overrightarrow{c_{1}}_{76}$ $\overrightarrow{c_{1}}_{24}$	74
3	Ph 🔨	Ph Cl	Ph 96 : 4 PK CI	80
4	Ph	~ Ci		78
5	ci 🔨	Ph Cl		85
6	c'\C	° ci		80
7	Ph0	Ph Cl	Pho O Ph	85
8	Ph0	CI		80
9	\bigcirc	Ph Cl		87
10		CI	Ci Ko	81
11	K K	Ph Cl	Cl Cl	78
12	K	CI	de la	72

Table : Co(II)Cl, catalysed acylative cleavage of oxiranes

a) Yield of isolated products. b) All the products were properly characterised by $^{1}\mathrm{H}$ NMR and IR and the ratio of regioisomers determined by $^{1}\mathrm{H}$ NMR of crude products. c) No cleavage is observed without Co(II)Cl₂ even after 12 hrs.

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