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Cobalt (II) Chloride Catalysed Regioselective Cleavage of Oxiranes with Chlorotrimethylsilane

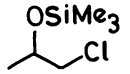
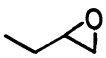
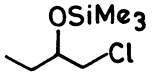
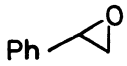
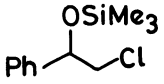
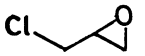
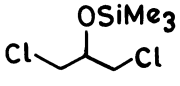
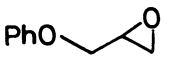
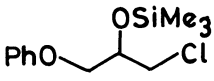
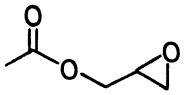
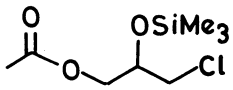
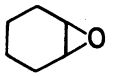
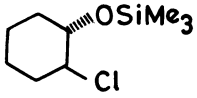
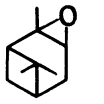
Javed IQBAL* and Mohd. AMIN KHAN
Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

Oxiranes can be cleaved regioselectively with chlorotrimethylsilane in presence of cobalt(II) chloride to the corresponding O-silylated vicinal chlorohydrins in excellent yields.

Regioselective cleavage of oxiranes[1] by halosilanes is an extremely mild and useful method for gaining access to O-silylated vicinal halohydrins. Bromo and Iodotrimethylsilanes cleave oxiranes[1a,1b] without a catalyst whereas nucleophilic catalyst is required if chlorotrimethylsilane[1c] is used for such a cleavage. In case of chlorotrimethylsilane mediated cleavage the regioselectivity is dependent upon the reaction temperature as the high selectivity is achieved only around -50 °C. We, now report that cobalt(II) chloride efficiently catalyses the cleavage[2] of a variety of oxiranes at ambient temperature with chlorotrimethylsilane in a highly regioselective manner.

Typically, oxirane (10 mmol) is added to a stirred solution of dry cobalt (II) chloride (≃ 30 mg) in dry acetonitrile (50 ml) and this is followed by a dropwise addition of chlorotrimethylsilane (12 mmol) over a period of 10 min. During this addition the temperature of the flask is maintained around 15 °C. The resulting mixture is stirred at ambient temperature for 1-2 h and the progress of reaction is monitored by TLC (diethyl ether-pet.ether). After the reaction is over the acetonitrile is evaporated and the residue taken into ether, washed with saturated sodium bicarbonate solution and water. Drying (Na_2SO_4) and evaporation of ether gave a liquid which on distillation yielded O-silylated halohydrins. A variety of oxiranes are cleaved under this condition in a highly regioselective manner to yield primary chlorides in excellent yields (see Table 1). Cyclohexene oxide and α-pinene oxide yielded only trans halohydrins in good yield (Table 1 entries 7 and 8). We are currently studying the mechanism of this reaction which may have some similarity with the $Co(I)H(CO)_4$ induced cleavage of cyclic ethers[3] as reported by Heck.

Table 1. Cobalt(II) Chloride Catalysed Cleavage of Oxiranes with Chlorotrimethylsilane

Entry	Oxirane[a]	Product	Yield/%[b,c]
1			73[d]
2			81
3			92
4			85
5			79
6			83
7			71
8			52

a) all the reactions were initially carried out at 15 °C during $ClSiMe_3$ addition.

b) yield of isolated product.

c) all compounds were properly characterized by ^1H NMR and IR.

d) this reaction was carried out at 0 °C.

References

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