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

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

Regioselective cleavage of oxiranes¹⁾ 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 cleavage²⁾ 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 ($\underline{\circ}$ 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 (Na₂SO₄) 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 ethers³⁾ as reported by Heck.

Entry	a) Oxirane	Product Yield/%	
1	∑ ⊳	OSIMe ₃ d)	
2	~~^o	OSiMe3 Cl 81	
3	Ph	OSiMe3 Ph-Cl 92	
4	cı	OSiMe3 CICI 85	
5	Ph0 0	OSiMe3 PhoCl 79	
6		O OSiMe3 Cl 83	
7	\bigcirc	Cl 71	
8	${\rm F}$	OSiMe ₃ ^{mm^cCl 52}	

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

- a) all the reactions were initially carried out at 15 ^OC during ClSiMe₃ addition.
- b) yield of isolated product.
- c) all compounds were properly characterized by $^{1}\mathrm{H}$ NMR and IR.
- d) this reaction was carried out at 0 $^{\circ}C_{\circ}$

References

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(Received April 14, 1988)