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Ring Opening Epoxides into Halohydrins with Elemental Iodine and Bromine in the Presence of Nano Catalyst ZrO_2

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ABSTRACT

There is a continued interest in the regioselective ring opening of oxiranes to the corresponding vicinal halohydrins. Although a variety of new and mild procedures to effect this transformation have been reported, most of them have some limitations.The ring opening of epoxides with elemental bromine and nano catalyst ZrO_2 affords vicinal bromo alcohols in high yields. This new procedure occurs regioselectively under neutral and mild conditions in various aprotic solvents even when sensitive functional groups are present.

Key words: Ring opening, epoxides, regioselective, bromine, nano catalyst, alcohols.

INTRODUCTION

There is a continued interest in the regioselective ring opening of oxiranes to the corresponding vicinal halohydrins. Although a variety of new and mild procedures to effect this transformation have been reported, most of them have some limitations[1]. The reaction is typically performed with hydrogen halides, but the harsh reaction conditions and the low observed regioselectivity in the opening of unsymmetrical epoxides have prompted a search for more selective and milder procedures. Recently, it has been found that epoxides can be converted into halohydrins by means of elemental halogen[2], but this method has limitations such as low yield, long reaction times, low regioselectivity and formation of acetonide byproducts in addition to the expected iodo adduct. Furthermore, iodination does not occur in aprotic solvents other than acetone.

In conjunction with ongoing work in our laboratory on the synthesis and formation of complex heterocyclic compounds containing donor nitrogen atoms, with neutral molecules such as iodine,[3-5] we found out that ZrO_2 with frame nano efficiently catalyzed the addition of elemental bromine to epoxides under mild reaction conditions with high regioselectivity (Scheme 1).

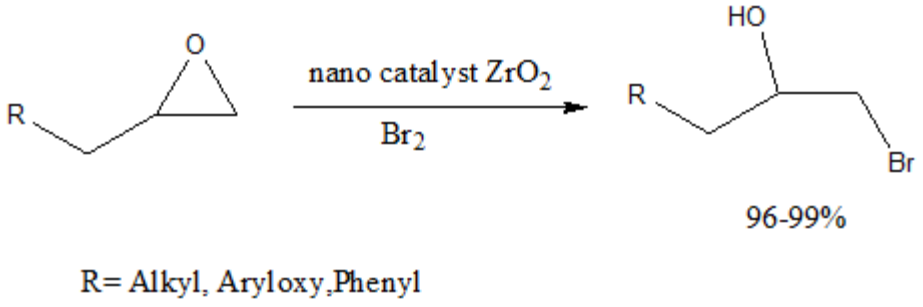
EXPRIMENTAL

NMR spectra were recorded by a Bruker Avance 300 MHz pectrometer locked on deuterium from solvent. Chemical shifts (*d* [ppm]) were calculated from chemical shift of deuterium lock and were not calibrated. FTIR spectra were measured on Perkin Elmer 2000 spectrometer in KBr pellets (1/200).

Epoxide (1 mmol) in CH2Cl2 (5 mL) was added to a stirred ZrO_2 catalyst (0.15 mmol) in at room temperature. Next, a solution of elemental Bromine (1 mmol) in CH2Cl2 (5 mL) was added portion-wise (15 min) to the above mixture. The progress of the reaction was monitored by TLC. After complete disappearance of the starting material, the reaction mixture was washed with 10% aqueous Na2S2O3 (2×10 mL) and water (2×10 mL). The aqueous layer was extracted with CH2Cl2 (2×10 mL).The combined organic layer was dried over anhydrous MgSO4 and evaporated to give crude alcohol–catalyst.

RESULTS

In this study, we wish to report the results of the reactions of some epoxides with elemental bromine and Iodine in the presence of a sub-stoichiometric amount of ZrO_2 (Scheme 1, Table 1).



Scheme 1: Synthesis bromohydrin by ZrO

Table 1: Ring opening 3-phenoxy-1,2-epoxypropane

Entry	Solvent	(%mol) catalyst	Time(h)	Isolate yield (%)
1	-	10	6	50
2	THF	10	8	50
3	MeOH	10	8	30
4	EtOH	10	8	25
5	CCl_4	10	8	30
6	CH_3CN	10	5	50
7	H_2O	10	24	trace
8	CH_2Cl_2	10	10min	80
9	CH_2Cl_2	15	5min	98
10	CH_2Cl_2	20	5min	98

The crude products were purified on a column of silica gel. The solvent was evaporated and pure halohydrin was obtained. The halohydrins obtained throughout this procedure were identified by comparison, where possible, with authentic samples prepared in accordance with literature procedures.

1-Bromo -2-boutanol (99%)

^{1}HNMR ($CDCl_3$, 300MHz) δ 0.95 (t, 3H, J=7.2Hz), 1.55-1.7 (m, 2H), 3.05-3.25(m, 1H), 3.3-3.5 (m, 1H), 3.75-3.8(m, 1H).; MS(EI) M/Z 200(M^+)

2-Bromo Cyclohexanol (97%)

^{1}HNMR ($CDCl_3$, 300MHz) δ 1.2-1.6(m, 4H), 1.8-1.9 (m, 1H), 2.0-2.2(m, 2H), 2.4-2.5(m, 1H), 3.5-3.65(m, 1H), 3.95-4.05(m,1H);MS(EI) M/Z 226(M^+); IR(KBr) 3425, 2960 cm^{-1}

2- Bromo -1-(4-Cholrophenyl)ethanol (96%):

^{1}HNMR ($CDCl_3$, 300MHz) δ 2.45(br, 1H), 3.45-3.5 (m, 2H), 4.80-4.88(m, 1H), 7.2-7.4(m, 4H);MS(EI) M/Z 282(M^+); IR(KBr) 3460, 2960 cm^{-1}

2- Bromo -1-phenyl ethanol (98%)

^{1}HNMR ($CDCl_3$, 300MHz) δ 2.50(br, 1H), 3.39-3.5 (m, 2H), 4.75(m, 1H), 7.25-7.4(m, 5H);MS(EI) M/Z 248(M^+); IR(KBr) 3398 , 2960 cm^{-1}

1- Bromo -3-(4-methoxyphenyl)2-propanol (98%)

pale yellow liquid, ^{1}HNMR ($CDCl_3$, 300MHz) δ 2.05(br, 1H), 2.85(d, 2H, J=6.2, 9.2Hz), 3.25 (dd, 1H, J=4.8,9.2 Hz), 3.35 (dd, 1H, J=3.8,9.2Hz), 3.6-3.75(m, 1H), 3.80(S, 3H),6.85(d, 2H,J=8.2Hz), 7.15(d, 2H, J=8.2Hz); ^{13}CNMR ($CDCl_3$ 50Hz) δ 14.67, 41.66, 55.10, 71.62, 113.92, 128.98, 130.12, 158.25;MS (EI) M/Z 292 (M^+); IR(KBr) 3560, 3050, 2960 cm^{-1}

1- Bromo -3-(4-acetylphenoxy)2-propanol (99%)

yellow Solid, mp 68-70^{0}C, ^{1}HNMR ($CDCl_3$, 300MHz) δ 2.55(S, 3H), 3.30-350 (m,2H), 3.90-4.05 (m, 3H), 6.90(d, 2H,J=7.8Hz), 7.9(d, 2H, J=7.8Hz);^{13}CNMR ($CDCl_3$ 50Hz) δ 8.84, 26.21, 69.12, 70.15, 114.66, 130.64, 162.75, 196.96; MS (EI) M/Z 320 (M^+); IR(KBr) 3460, 3020, 2970, 1710 cm^{-1}

1- Bromo -3-(4-Cholorophenoxy)2-propanol (97%)

^{1}HNMR ($CDCl_3$, 300MHz) δ 2.40 (br, 1H), 3.35-3.40 (m,2H), 3.45-3.50 (m, 1H), 3.95-4.0 (m, 1H), 4.05-4.10(m, 2H), 6.85(d, 2H, J=8.2 Hz), 7.15(d, 2H, J=8.2 Hz); MS (EI) M/Z 312 (M^+); IR(KBr) 3515 cm^{-1}

1-Bromo-3-phenoxy-2-propanol(98%)

^{1}HNMR ($CDCl_3$, 300MHz) δ 2.40(br, 1H), 3.30-3.55 (m, 2H), 3.8-4.1(m, 3H), 6.75-7.0(m, 3H) 7.15-7.35(m,2H);MS(EI) M/Z 278(M^+); IR (KBr) 3500 , 2985 cm^{-1}

DISCUSSION

In conclusion, this new method appears to be highly competitive with the other methods reported in the literature. The reaction occurs in neutral and mild conditions on the acid-sensitive substrates and vicinal halohydrins were obtained in high yields and region-selectivity. In addition, in comparison with our previous methods, ZrO_2 is cheaper, less step need for preparation, and overall yield is higher.

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