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Pd-CATALYSED REGIOSPECIFIC REDUCTIVE RING OPENING OF EPOXIDES AND GLYCIDIC ESTERS+

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Abstract: The regiospecific ring opening of epoxides was achieved by Pd-catalysed transfer hydrogenolysis using ammonium formate as hydrogen source.

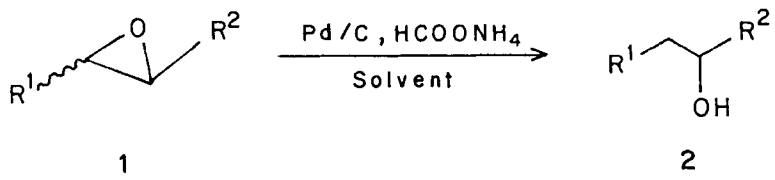
Epoxides are very important chiral building blocks in organic synthesis and can easily undergo stereospecific ring opening reactions to form bifunctional compounds[1]. The selective reduction of epoxides and glycidic esters represents one of the most direct methods to obtain hydroxy compounds. A variety of reducing agents such as $LiAlH_4$[2], $LiAlH_4$-$AlCl_3$[3], $NaBH_4$[4], $LiBHEt_3$[5], $NaBH_3CN$-BF_3[6], B_2H_6-morpholine[7], $NaBH_4$-BH_3[8], NaH-RONa-metal salts[9], Li or Na in liq. NH_3[10], Zn-Me_3SiCl[11], H_2-Pd, Ni or Pt[12] and

+ NCL Communication No. 5931

SmI_2[13] have been reported in the literature to accomplish the reductive ring opening of epoxides. While the nucleophilic hydride transferring reagents upon reaction with epoxides generally afford the more highly substituted alcohol, a dramatic reversal in selectivity is often observed in the case of Lewis acid modified hydride reagents to produce the less substituted alcohol, but mixtures usually result[14]. Moreover, the high temperatures and pressures coupled with isomerisation and rearrangement of epoxides often associated with the conventional catalytic hydrogenation methods make them less attractive in organic synthesis.

Recently, catalytic transfer hydrogenation with Pd/C as catalyst and ammonium formate as hydrogen source has found widespread use in the reduction of various functionalities[15]. We wish to report, in this communication, a new method for selective ring opening of epoxides and glycidic esters under transfer hydrogenation conditions in high yields (Scheme - 1).

Several examples illustrating this novel and efficient procedure for reductive ring opening of epoxides are presented in Table - 1. Evidently, epoxides and glycidic esters with R=Ar undergo reductive ring opening exclusively at the benzylic position in excellent yields (entries 1-3 and 7). In



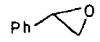
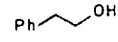
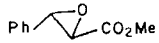
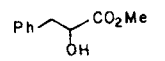
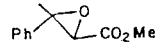
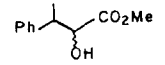
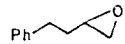
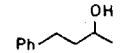
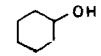
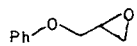
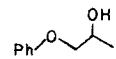
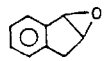
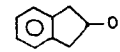
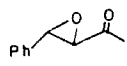
1 2

R^1 = Alkyl , Aryl

R^2 = H , CO_2Me

SCHEME – I

TABLE 1 : Pd-CATALYZED TRANSFER HYDROGENATION OF EPOXIDES TO ALCOHOLS

ENTRY	SUBSTRATES	TIME h	SOLVENT	PRODUCTS [a]	YIELD (%) [b]
A		2	MeOH		100
B		3	MeOH		95
C		3	MeOH		95 [c]
D		18 [d]	MeOH		80
E		18 [d]	MeOH		50
F		3	Dioxan		70
G		3	Dioxan		55
H		20	MeOH	—	—

a Well characterized by IR , ^1H and ^{13}C NMR ; b Isolated yield ;

c syn / anti = 1:2 as determined from ^1H NMR ; d at 45 °C ; for others , reflux temperatures

contrast, it may be noted that the aliphatic epoxides underwent regiospecific ring opening at the less hindered carbon to afford the corresponding alcohol in high yields. However, the epoxy ketone (entry 8) under the reaction conditions gave mixtures of products which were difficult to separate and characterise. The structure of regiosomers was confirmed by ^{1}H and ^{13}C NMR[16].

It may be mentioned that esters having a hydroxyl function at the α or β position not only constitute an important class of natural products but also serve as useful intermediates in organic synthesis[17]. The regiospecific ring opening of glycidic esters by transfer hydrogenolysis, thus, offers one of the most efficient methods to make α -hydroxy esters.

In conclusion, the results described herein, demonstrate the novelty of Pd-C catalyst exercising unique selectivity in the reductive ring opening of epoxides and glycidic esters under transfer hydrogenation conditions using ammonium formate as hydrogen source.

Experimental Procedure

In a typical reaction, a mixture of styrene oxide (0.6 g, 5mM), ammonium formate (0.63 g, 10 mM) and 5% Pd/C(0.05 g) in MeOH (15 mL) was refluxed for 2 h. The progress of the reactions was monitored by TLC. After

the reaction was complete, the catalyst and other inorganic solids were filtered off and the filtrate concentrated to afford β -Phenethyl alcohol (0.61 g, 100 %) in virtually pure form.

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16. Spectral Data for Selected Products:

2C: IR(Neat): 3450, 2960, 1735, 1450, 1130, 720 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$,): syn/anti = 1:2, 1.35 [3H, d, J=7Hz, CH_3(anti isomer)], 1.45[3H, d, J=6Hz, CH_3(syn isomer)], 3.25 (1H, m, benzylic H), 3.72 (3H, s, COOMe), 3.82 (3H, s, COOMe), 4.35 (1H, m, CHOH); ^{13}C NMR (200 MHz, $CDCl_3$,): syn/anti mixture; 14.7 and 17.6 (Me), 43.4 and 43.5 (ArCH), 52.1 and 52.3

(CHOH), 75.1 and 75.2 (OMe), 126.8, 127.1, 128.1, 128.3, 140.8, 142.6 (aromatic C), 174.6 (C=O). **2G:** ^{1}H NMR (200 MHz, $CDCl_3$,): 2.2 (1H, bs, OH), 2.9 (2h, dd, J=14 Hz and 3 Hz, CH_2), 3.25 (2H, dd, J=14 Hz and 6 Hz, CH_2), 4.15 (1H, quintet, CHOH), 7.25 (4H, m, ArH).

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