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ARTICLE *in* ULTRASONICS SONOCHEMISTRY · SEPTEMBER 2005

Impact Factor: 4.32 · DOI: 10.1016/j.ultsonch.2004.08.002 · Source: PubMed

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Ultrasonic activated efficient method for the cleavage of epoxides with aromatic amines

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Received 5 January 2004; received in revised form 2 August 2004; accepted 5 August 2004
Available online 19 January 2005

Abstract

An improved protocol for the cleavage of epoxides with aromatic amines in the presence of $FeCl_3$ promoted by ultrasonic irradiation. This new methodology provides excellent yields in short reaction times (15–25 min) at room temperature.

Keywords: Epoxide ring opening; Ultrasound; Aromatic amines; Regioselectivity; β-Amino alcohols

1. Introduction

β-Amino alcohols are an important class of organic compounds, which have found much use in medicinal chemistry [1]. Classically, these have been synthesized by opening of the epoxide ring with an excess of amine at elevated temperatures. Since the high temperature may not be ideal for certain functional groups, a variety of methods have been developed in the literature to carry out the epoxide ring opening at room temperature [2]. To obviate the above said limitations, a variety of promoters have been employed which include $Ti(OPr)_4$ [3], SmI_2 [4], basic metal amides [5], and metal Inflates [6]. Usually, these promoters are associated with several drawbacks, for example in case of metal amide, the epoxide frequently undergoes rearrangement to give allyl alcohol as the major product [5]. Further, primary amines show almost no regio-selectivity in case of basic metal amide salts [5]. Moreover, benzylic and aliphatic amines do not react under $CoCl_2$ catalyzed opening of epoxide [2–5]. Hence, there is a need for the development of newer versatile methods that could overcome most of the above shortcomings.

One of the most fascinating developments in organic synthesis during the recent years is the application of ultrasound [7] over the conventional thermal heating for organic reactions. In recent years a large number of organic transformations have been reported using ultrasonics [8]. It is well documented in the literature that the ultrasonic irradiation not only accelerates chemical reactions but also reduces the number of steps, which are required for normal reactions. The application of ultrasound has gained popularity among synthetic organic chemists not only to improve classical organic reactions by shortening reaction times and/or improving yields, but as well to promote new reactions [9].

2. Experimental

2.1. General

Melting points are recorded on Electro-thermal melting point apparatus and are uncorrected. IR spectra were recorded on Perkin–Elmer 683 using KBr pellets;

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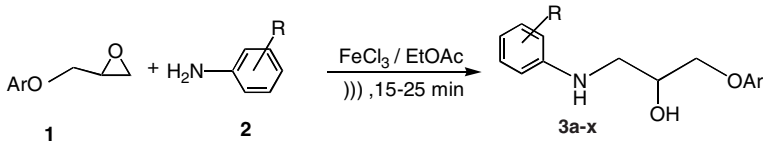
doi:10.1016/j.ultsonch.2004.08.002



Scheme 1.

mass spectra recorded on VG 7070H Micromass mass spectrometer, and ^{1}H NMR spectra on Bruker 200 MHz spectrometer.

2.2. Chemicals

All chemicals were of research grade and were used as obtained from Aldrich, Lancaster, Fluka or local available makes.

2.3. Typical procedure for sonochemical cleavage of epoxides with aromatic amines

To a solution of epoxide (0.1 mmol) in ethyl acetate (3 ml), was added amine (0.1 mmol) and $FeCl_3$ (0.05 mmol).This reaction mixture was sonicated in a thermostated (30 °C) ultrasonic cleaning bath (Elma TP680DH) at 40 kHz. The ultrasonic cleaner had a power supply of 480 W and the tank dimensions were 505 mm × 137 mm × 100 mm with liquid holding capacity of 6.9l. After the completion of reaction as indicated by TLC (precoated glass plates by GF_{254} silica gel with fluorescent indicator employing hexane–ethyl acetate, 8:2) the reaction mixture was filtered and the filtrate was washed with water and extracted with ethyl acetate. Evaporation of ethyl acetate afforded crude product, which was subjected to column chromatography (silica gel, 60–120 mesh) using hexane–ethyl acetate (9:1) as eluent to obtain the pure products.

3. Results and discussions

In our earlier studies, we have reported several biocatalytic methods for the enantioselective cleavage of epoxides [10]. Further we have also been successful in utilizing ultrasound to various biocatalytic [11] and organic transformations [12]. In continuation of these efforts, it was considered of interest to investigate the ring opening of different aryloxy epoxides with amino nucleophiles, particularly aryl amines. Herein, we wish to report a facile and efficient cleavage of epoxide rings

Table 1
Ultrasound activated efficient synthesis of β-amino alcohol

Product (**3**)	Ar	R	Time (min)	Yield (%)[a]	Melting points (°C)
a	C_6H_5	4-NO_2	25	90	54–55
b	C_6H_5	3-NO_2	22	95	101–102
c	C_6H_5	2-NO_2	23	88	63–64
d	C_6H_5	4-Br	20	92	–
e	C_6H_5	2-CN	23	89	76–77
f	C_6H_5	4-CH_3	21	85	57–58
g	C_6H_5	$CH(CH_3)_2$	17	93	–
h	C_6H_5	iso-Bu	19	90	–
i	$C_{10}H_7$	4-NO_2	22	92	72–74
j	$C_{10}H_7$	3-NO_2	21	93	67–69
k	$C_{10}H_7$	2-NO_2	23	88	96–97
l	$C_{10}H_7$	4-Br	24	85	–
m	$C_{10}H_7$	2-CN	25	90	108–109
n	$C_{10}H_7$	4-CH_3	23	87	130–131
o	$C_{10}H_7$	$CH(CH_3)_2$	15	90	–
p	$C_{10}H_7$	iso-Bu	19	90	109–110
q	*p*-ClC_6H_4	4-NO_2	23	90	67–68
r	*p*-ClC_6H_4	3-NO_2	22	87	70–72
s	*p*-ClC_6H_4	2-NO_2	21	90	115–116
t	*p*-ClC_6H_4	4-Br	20	88	–
u	*p*-ClC_6H_4	2-CN	22	85	88–89
v	*p*-ClC_6H_4	4-CH_3	25	85	71–72
w	*p*-ClC_6H_4	$CH(CH_3)_2$	18	92	57–58
x	*p*-ClC_6H_4	iso-Bu	18	90	–

[a] Isolated yields.

with aromatic amines to produce β-amino alcohols in the presence of $FeCl_3$ under ultrasonic conditions for the first time (Scheme 1). However, there are reports on the use of $FeCl_3$ as a catalyst for the alcoholysis of epoxides [13,14].

In this pursuit we first examined the reaction of 3-phenoxy-1,2-epoxy propane (**1**) with 4-nitroaniline (**2**) in the presence of $FeCl_3$ promoted by ultrasound in ethyl acetate to give the corresponding β-amino alcohol (**3a**) in excellent yield (90%). This finding has led to us exploit the generality of the reaction to other epoxides with different amines Table 1. As seen from the results, a number of aromatic amines have been employed for the cleavage of different epoxides particularly ring deactivated amines such as 4-bromoaniline, 3-nitroaniline, 2-nitroaniline and 2-cyanoaniline. It has been observed from the literature that there is a limited success for the cleavage of epoxides by such aromatic amines. Whereas the present methodology has been found successful in the ring cleavage of epoxides by 4-nitroaniline [15]. Further, in this process the reaction takes about 15–25 min unlike the reported methodologies, which take longer reaction times for the cleavage of epoxides [4]. It is interesting to observe that this methodology is applicable to the cleavage of epoxides by alkyl amines, for example, entries **g** and **h**. This reaction has also been carried out in the absence of ultrasound and it is found that it takes about 7–8 h for about 70% conversion, thus exhibiting the effect of ultrasound in this process. It is presumed that the opening of the epoxide group with the amino functionality in the presence of ultrasonic irradiation is facilitated by acoustic cavitation in the reaction medium Thus β-amino alcohols are obtained in the higher yields by enhanced rate of reaction in the presence of ultrasound.

4. Conclusion

In summary, we have developed an efficient protocol for cleavage of epoxide with aromatic amines in the presence of $FeCl_3$ promoted by ultrasound. This methodology is applicable to a variety of aromatic amines especially ring deactivated aromatic amines to afford the corresponding cleavage products in high yields under mild conditions. We are presently attempting to broaden the scope of this process to other nucleophiles and epoxides and study the influence of ultrasound as well as the nature of catalyst.

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