

Facile Conversion of Epoxides to 1,2-Diacetates with NaOAc·3H₂O/Ac₂O System

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ABSTRACT: This study represents a highly efficient and regioselective ring-opening of epoxides with acetic anhydride in the presence of NaOAc·3H₂O at solvent-free conditions. The ring-opening of different classes of epoxides were carried in oil bath (70-80 °C) to afford 1,2-diacetates in high to excellent yields.

KEY WORDS: Ac₂O; 1,2-Diacetates; Epoxides; NaOAc·3H₂O; Ring-opening.

INTRODUCTION

Epoxides have become very popular in organic synthesis not only as building blocks but also as synthetic intermediates [1-3]. They are capable to react with various nucleophiles to afford 1,2-difunctional products. Among these, 1,2-diols and 1,2-diacetoxy esters possesses valuable synthetic utilities [4]. 1,2-Diols are prepared in a straightforward method by Lewis or Brønsted acid catalysis of ring opening of epoxides with water. Therefore by subsequent acetylation of 1,2-diols with acetyl chloride, 1,2-diacetoxy esters are prepared in a two step procedure. In contrast, the preparation of 1,2-diacetates is also carried out by direct conversion of epoxides to these compounds. The literature review shows that most of the reported methods are devoted to one-pot approach because of the simplicity and high yields. In this context, the direct conversion of epoxides to 1,2-diacetoxy esters has been achieved by the reaction of epoxides with acetic anhydride in the presence of HCl-ZnCl₂ [5], BF₃·Et₂O [6], DBU-LiCl [7], *n*-Bu₄NCl [8], *n*-Bu₄NOAc [9], Bu₃P [10], LiClO₄ [11], Er(OTf)₃ [12], HY zeolite [13], (NH₄)₃PMo₁₂O₄₀ [14], (TBA)₄PFeW₁₁O₃₉·3H₂O [15], ZrO(OTf)₂ [16],

NaBH₄ [17], phosphomolybdic acid or its supported on silica gel [18] and molecular sieves 4 Å [19]. Though, most of the mentioned protocols are efficient and useful, however, they generally suffer from using expensive reagents, strongly acidic/basic reaction conditions, long reaction times and limitation to use both aromatic and aliphatic epoxides as starting materials.

On the other hand, the challenge in chemistry to develop efficient processes, reaction media, conditions and utility of materials based on the idea of green chemistry is one of the most important issues in scientific community. Herein, we wish to report a simple and efficient method for conversion of structurally different epoxides to the corresponding 1,2-diacetoxy esters using NaOAc·3H₂O/Ac₂O as an inexpensive and environmentally benign reagent system (Scheme 1).

EXPERIMENTAL SECTION

Materials and Methods

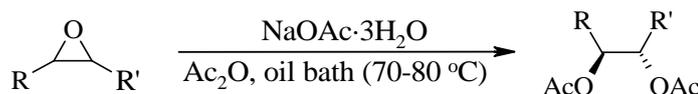
All reagents and substrates were purchased from Merck Company with the best quality and they were used without further purification. FT-IR and ¹H, ¹³C NMR

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Scheme 1: Ring-opening of epoxides with NaOAc : 3H₂O/Ac₂O system.

Table 1: Optimization experiments for solvent-free conversion of styrene oxide to 1,2-diacetoxy-1-phenylethane with sodium acetate/acetic anhydride system.

Entry	Reaction components	Molar Ratio	Condition ^a	Time (h)	Conv. (%)
1	Epoxide/Ac ₂ O/NaOAc (anhydrous)	1:3:3	oil bath	2	0
2	Epoxide/Ac ₂ O/NaOAc·3H ₂ O	1:3:1	r.t.	2	30
3	Epoxide/Ac ₂ O/NaOAc·3H ₂ O	1:3:1	oil bath	2	55
4	Epoxide/Ac ₂ O/NaOAc·3H ₂ O	1:3:2	oil bath	2	100

^aTemperature of oil bath was 70-80 °C.

spectra were recorded on Thermo Nicolet Nexus 670 FT-IR and Bruker Avance 300 MHz spectrometers, respectively. The products were characterized by FT-IR and ¹H, ¹³C NMR techniques and compared with the reported data in literature. All yields refer to isolated pure products. TLC was applied for the purity determination of the substrates, products and for monitoring of the reactions over silica gel GF254 aluminum sheet.

Conversion of Epoxides to 1,2-Diacetates with NaOAc·3H₂O/Ac₂O System: A General Procedure

In a round-bottomed flask (10 mL) equipped with a magnetic stirrer, a solution of epoxide (1 mmol) and acetic anhydride (3 mmol) was prepared. NaOAc·3H₂O (2 mmol) was then added and the reaction mixture was stirred in oil bath (70-80°C) for 2 h. After completion of the reaction, an aqueous solution of NaHCO₃ (5%, 5 mL) was added and the mixture was stirred for additional 10 min. The mixture was extracted with EtOAc (2 × 5 mL) and then dried over anhydrous sodium sulfate. Evaporation of the solvent and a short column chromatography of the resulting crude material over silica gel (EtOAc/*n*-hexane: 2/5) afforded the pure liquid 1,2-diacetate in 85-96% yield (Table 2). Spectral data for 1,2-diacetoxy-1-phenylethane is exemplified: ¹H NMR (CDCl₃, 300 MHz) δ 7.40-7.31 (m, 5H), 6.02 (dd, *J* 4.2, 7.8 Hz, 1H), 4.39-4.25 (m, 2H), 2.10 (s, 3H), 2.06 (s, 3H); ¹³C NMR (CDCl₃, 75.5 MHz) δ 170.64, 170.05,

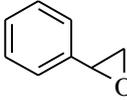
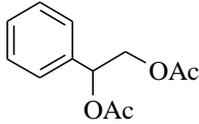
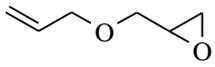
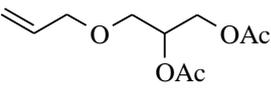
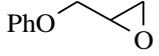
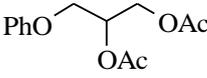
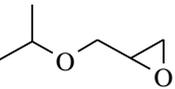
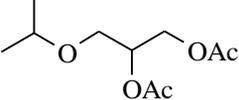
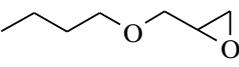
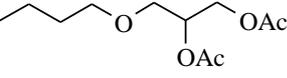
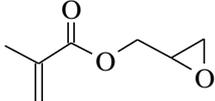
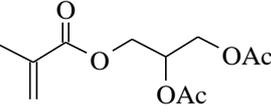
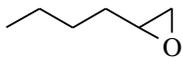
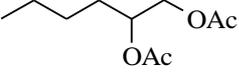
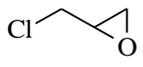
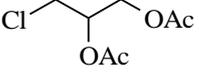
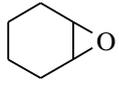
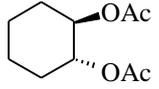
136.50, 128.64, 128.63, 126.70, 73.32, 66.09, 21.10, 20.78; FT-IR (ν_{max}/cm⁻¹, neat): 3033, 2954, 1744, 1604, 1455, 1372, 1241, 1046, 1012, 950.

RESULTS AND DISCUSSIONS

Transformation of epoxides to 1,2-diacetoxy esters was first examined by the reaction of styrene oxide with acetic anhydride in the presence of anhydrous NaOAc. The results showed that under different conditions the reaction did not any take place and styrene oxide was recovered from the reaction mixture. However, performing of the reaction with sodium acetate trihydrate, exhibited the more efficient result. Further experiments resulted that using 2 mmol NaOAc·3H₂O is the requirement for complete reaction of styrene oxide (1 mmol) with Ac₂O (3 mmol). The reaction was carried out under oil bath conditions (70-80 °C) within 2 h to give 1,2-diacetoxy-1-phenylethane in 96% yield (Table 1, entry 4). Encouraged by the result, the capability of this synthetic method was more studied with the reaction of various epoxides containing electron-releasing or withdrawing groups with Ac₂O under the optimized conditions. Table 2 shows the general trend and versatility of this synthetic method. As it's seen, all reactions were carried out successfully within 2-3 h at solvent-free conditions to give the products in high to excellent yields.

The suitability and advantage of this synthetic method was highlighted by comparison of the reaction of styrene

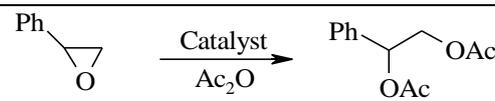
Table 2: Conversion of epoxides to 1,2-diacetates with NaOAc·3H₂O/Ac₂O system^a.

Entry	Epoxide	1,2-Diacetate	Time (h)	Yield (%) ^b	Ref.
1			2	96	18
2			2	94	18
3			3	96	18
4			2	93	18
5			2	92	18
6			2	96	18
7			2	85	13
8			2	90	18
9			2	91	18

a: All reactions were carried out with the molar ratio of epoxide/Ac₂O/NaOAc·3H₂O (1:3:2) under oil bath conditions (70-80 °C).

b: Yields refer to isolated pure products.

Table 3: Comparison of the conversion of styrene oxide to 1,2-diacetoxy-1-phenylethane promoted by NaOAc·3H₂O and other reported reagents.

						
Entry	Catalyst	Mol%	Condition	Time (h)	Yield (%)	Ref.
1	NaOAc·3H ₂ O	200	70-80 °C	2	96	–
2	PMA	1	r.t.	0.25	95	18
3	PMA-SiO ₂	5	r.t.	0.08	98	18
4	MS 4 Å	0.15 g	reflux	2	90	19
5	NaBH ₄	20	reflux	1.5	96	17
6	Bu ₄ NCl	5	reflux	3	83	8
7	HY Zeolite	0.05 g	r.t.	12	90	13
8	Bu ₃ P	10	reflux	24	98	10
9	Er(OTf) ₃	0.1	r.t.	2	0	12
10	ZrO(OTf) ₂	0.75	50 °C	1 min	99	16
11	LiClO ₄	50	r.t.	2-5	66	11
12	(NH ₄) ₃ PMo ₁₂ O ₄₀	10	r.t.	1	98	14

oxide with acetic anhydride promoted with NaOAc·3H₂O and other reported reagents (Table 3). A case study shows that in viewpoints of the availability, cheapness of the catalysts and yield of the product, NaOAc·3H₂O shows a more or comparable efficiency towards the other reagents.

CONCLUSIONS

In summary, we have shown that NaOAc·3H₂O/Ac₂O system easily and efficiently promoted direct conversion of epoxides to 1,2-diacetates under oil bath conditions (70-80 °C). The reactions were completed within 2-3 h to afford the products in high yields. The cheapness and availability of the reagents, manipulation to a wide range of epoxides and high efficiency as well as the benefits of solvent-free conditions are the advantages which make this protocol a synthetically useful addition to the present methodologies.

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