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LiBr/*β*-CD/IBX/H_2O-DMSO: A New Approach for One Pot Biomimetic Regioselective Ring Opening of Chalcone epoxides to Bromohydrins and Conversion to 1,2,3-Triketones

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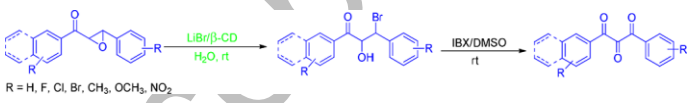
Abstract

Highly regioselective ring cleavage of chalcone epoxides to bromohydrins has been carried out in good yields with LiBr in presence of *β*-CD using DMSO-H_2O as solvent system. The ring opened product i.e. bromohydrin were well adapted to IBX mediated oxidation in such a fashion that the bromohydrins are transformed to their corresponding 1,2,3-triketones in moderate to good yields in one-pot.

GRAPHICAL ABSTRACT:



KEYWORDS: Chalcone epoxide, Bromohydrin, *β*-Cyclodextrin, IBX, Triketones

1. INTRODUCTION

Chalcone epoxides are important and versatile synthetic intermediates used as starting material in different organic transformations to form the molecules of pharmaceutical importance.[1] Due to ring strain in epoxides, they go through easy intra- and

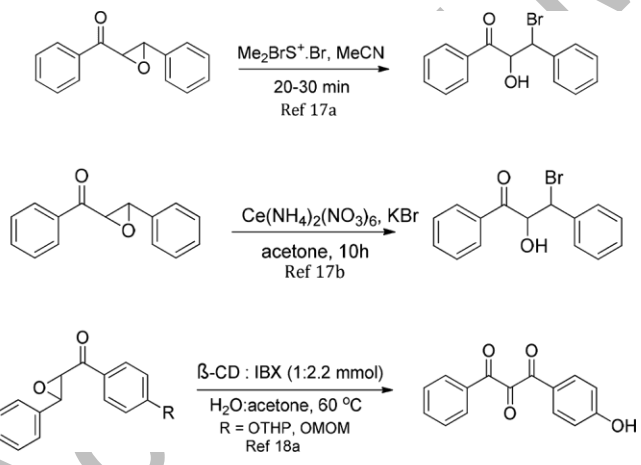
intermolecular nucleophilic addition reaction resulting into the formation of various regio- and stereo-selective synthons under mild catalytic conditions.[2–5]

vic-Halohydrins are valuable precursors in various useful synthetic transformations such as in the synthesis of halogenated marine bioactive natural products.[6, 7] The ring cleavage of oxiranes to form halohydrins are usually executed with elemental halogens,[8] hydrogen halides,[9] Lewis acids[10] and metal halides.[11] However, many of the reported methods are limited by unsatisfactory yields, side products formation, long reaction times, competing rearrangements, harsh reaction conditions and low regioselectivity.

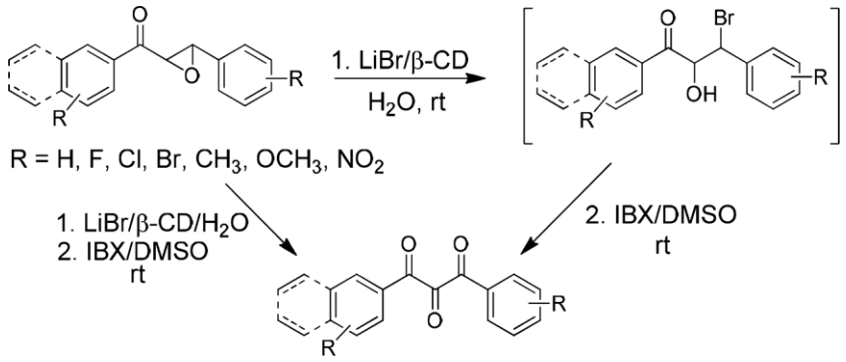
1,2,3-Tricarbonyls have gained attention among the organic chemists ever since the first synthesis of diphenyl triketone in 1890 by von Pechmann and de Neufville.[12] Rubin, and Wasserman[13] have widely studied the chemistry of these compounds. *vic*-Tricarbonyl compounds are the key structural building blocks in biologically active natural products, [14] such as the potent immunosuppressant FK-506, [14a-c] Rapamycin, [14d] and 29-demethoxyrapamycin, [14e] protease inhibitor molecules and other biologically active compounds[15] in synthetic organic chemistry. Vicinal tricarbonyl compounds, characterized by the highly electrophilic nature of the central carbonyl group, can be easily attacked by variety of nucleophiles. Several methods have been reported for their synthesis but many of these involve additives, extra steps to synthesize precursors and also require strong oxidizing agents to complete this reaction.[12, 13] Moreover, some of them suffer from low conversions and poor selectivity. Hence, there is still scope for a generally applicable and mild method, preferably using through supramolecular catalysis

involving cyclodextrins due to the fine tuning of their physicochemical properties which is continuously attaining importance in the contemporary organic transformations. These reactions do not produce any toxic waste products. Cyclodextrins are cyclic oligosaccharides having hydrophobic cavities and exert micro-environmental effects in catalyzing reactions through non-covalent hydrogen bonding forming reversible host–guest complexes just like in enzymes. [16] In our previous study,[16b, 18a] we have developed one-pot deprotection of THP/MOM ethers and concomitant oxidative cleavage of epoxides to form 1,2,3 triketones using β-Cyclodextrin/IBX. In continuation of our recent studies with *β*-CD/IBX[18] we conceived the possibility of converting chalcone epoxides[21] to their corresponding tricarbonyl compounds in a simple manner.

Previous work: [17, 18a]



This work:



To our delight, herein, we devise that LiBr/*β*-CD in water can be conveniently utilized to achieve the conversion of chalcone epoxides[21] to their corresponding bromohydrins in good to excellent yields under mild reaction conditions. Further, we establish that this methodology can be conveniently combined with the alcoholic oxidation and oxidative debromination reaction of bromohydrins by IBX in DMSO to access 1,2,3-triketones in one pot.

This reaction was conducted by the in situ formation of the epoxide-*β*-CD complex followed by the nucleophilic attack of LiBr and stirring at room temperature to afford the corresponding bromohydrins in respectable yields. Indeed, we imagined this bromohydrins could be readily converted to their corresponding triketones in the same pot.

2. RESULTS AND DISCUSSION

2.1 Chemistry

We visualized that the IBX mediated conversion of bromohydrins to the *vic*-tricarbonyls could be readily adapted to one-pot transformations by capitalizing on the LiBr-mediated conversion of epoxides in H_2O:DMSO to the corresponding bromohydrins. Thus, the

chalcone epoxides were converted to bromohydrins with LiBr/*β*-CD in water, and the latter were subjected to IBX-mediated oxidation into the same pot. The chalcone epoxides were prepared by following the literature procedure.[18a]

From the results as shown in Table 1, in our preliminary study toward the development of this methodology, a prototype reaction was carried out by treating substrate **1a** with LiBr (1.2 mmol) and *β*-CD in DMSO at room temperature and only a small conversion of **1a** to **2a** was obtained even with prolonged reaction time (Table 1, entry 1, 25%). On the contrary, the yield of **2a** was enhanced abruptly when only water was used as a solvent (Table 1, entry 2, 82%). This is because of a lower solubility of *β*-CD in the DMSO than in the water. But, with the introduction of 1.2 mmol of LiBr and *β*-cyclodextrin as a supramolecular host along with 2.5 mmol of IBX in the reaction, to our delight, a small conversion of **1a** to **3a** was obtained to afford the product **3a** in 24% (Table 1, entry 3). The role of *β*-CD in this reaction may be that it complexes with the epoxide assisting the nucleophilic attack by LiBr, expedites the solubility of IBX in water and conducts the reaction smoothly. Surprisingly, the **4a** was obtained as the sole product[20] when only H_2O was used as a solvent (Table 1, entry 4, 80%). This suggests that DMSO is acting as an oxidant and found indispensable for the transformation of bromo to carbonyl functionality. During the exploratory studies conducted, this model reaction was attempted by examining the relative proportions of H_2O:DMSO. Among the proportions of H_2O:DMSO, (1:1) was found to be the best solvent system affording the highest yield (89%) of **3a** in the shortest reaction time (10 h) (Table 1, entry 7). Since, the v/v ratio of H_2O:DMSO employed can be as low as 1:1; therefore, the 1:1 v/v of H_2O:DMSO solvent

system was used in the standard conditions. For instance, on taking 3:1 of solvent ratio (H_2O:DMSO), product **3a** was obtained in 69% yield (Table 1, entry 5). It is also remarkable that decreasing the H_2O:DMSO ratio to 2:1 or 1:1 resulting into the enhancement of the product yield of **3a** to 78 and 89% respectively. The present optimized synthesis of **3a** involves stirring a mixture of **1a,** LiBr and *β*-CD at rt for 5 h in H_2O:DMSO (1:1) followed by the addition of IBX and stirring for a further 5–8 h at rt to afford triketones **3a** in consistently good yields (89%).

After getting optimization conditions in hand, we have extended the procedure to a variety of chalcone epoxides, which are tabulated in Table 2 and 3. They were easily converted into their respective bromohydrins and triketones in excellent yields (79-91%).

A mechanistic description of this transformation is depicted in Fig. 1. A plausible mechanism for the transformation of chalcone epoxides to triketones is proposed in Scheme 1. The role of *β*-CD seems to be not only to activate epoxide (**I**) by hydrogen bonding, but also to encourage highly effective ring opening by LiBr due to inclusion complex formation, thus assisting the hydrolysis to form bromohydrin (**II**). The transformation of (II) to (III) was almost imperceptible without the added IBX. This clearly shows the role of IBX in the conversion of (II) to (III). Upon monitoring of the reaction without added IBX, it is expected the formation of a salt resulting from the attack of DMSO (Kornblum oxidation) on (II). Its decomposition to (III) did not occur until IBX was not added which in turn generate product (**V**) via intermediates (**IV**). Compound (**V**) can be easily converted to (**VI**) through further oxidation with IBX.[19]

All products were established on the basis of NMR, FTIR and mass spectrometry (ESI†). For example, compound **2a**, the ^{1}H-NMR spectrum showed the characteristic broad peaks at δ 3.99 ppm for alcoholic hydroxyl group. The appearance of a broad peak at 3425 cm^{-1} for the –OH groups in the IR spectrum point out the cleavage of epoxide ring and confirm the formation of compound **2a**. In the IR spectrum of Compound **3a,** disappearance of peak at 3425 cm^{-1} of hydroxyl group confirm its formation. The appearance of the carbonyl groups showed stretching frequencies at 1695 and 1645 cm^{-1}. HRMS of **3a** supported a molecular composition of $C_{15}H_{10}NaO_3$ $[M+Na]^+$, representing 11 degrees of unsaturation. In the ^{1}H NMR spectrum of **3a**, disappearance of peaks at δ_H ppm 5.39 (d, *J* = 2 Hz, 1H), 5.24 (d, *J* = 2H, 1H) and 3.99 (s, 1H, D_2O exchangeable) establish its structure. In ^{13}C NMR spectrum, δ_c ppm 193.3 and 189.6 confirm the presence of two types of carbonyl group.

3. CONCLUSIONS

In conclusion, we have devised an elegant and alternative methodology for one pot conversion of chalcone epoxide to triketones *via* regioselective bromohydrin using a mild and eco-friendly catalytic system LiBr/*β*-CD/IBX in H_2O:DMSO solvent system under supramolecular catalysis. The conversion of chalcone epoxides to the tricarbonyl compounds described herein establishes a valuable addition to the repertoire of IBX mediated transformations. Thus, we have revealed the synthesis of highly valuable synthons bromohydrins, and 1,2,3-triketones directly from the easily accessible chalcone epoxides in moderate to good yields in one pot operation in a biomimetic fashion.

4. EXPERIMENTAL

All the required chemicals were purchased from Merck and Aldrich Chemical Company. Pre-coated aluminium sheets (silica gel 60 F254, Merck) were used for thin-layer chromatography (TLC) and spots were visualized under UV light.IR spectra were recorded with KBr on Thermo Nicolet FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded respectively on Bruker Spectrospin DPX 500 MHz and Bruker Spectrospin DPX 125 MHz spectrometer using $CDCl_3$ as a solvent and trimethylsilane (TMS) as an internal standard. Melting points were performed with Ambassador® and Digital Melting point apparatus (Nutronics), Popular India. Splitting patterns are designated as follows; s = singlet, d = doublet, m = multiplet, br = broad. Chemical shift (δ) values are given in ppm. High-resolution mass spectra (HRMS) were obtained on a Brüker micrOTOF™-Q II mass spectrometer (ESIMS).

4.1. General Procedure for Synthesis of Compounds

4.1.1. Conversion of Chalcone Epoxides to Bromohydrins (2a, 2b, 2f, 2i, 2k) (Table 2)

A solution of chalcone epoxide (1 mmol) and *β*-CD (1 mmol) in H_2O/DMSO (1:1) (10 mL) were added LiBr (1.2 mmol) and the mixture was stirred at room temperature. As soon as the starting material disappeared (as monitored by TLC analysis), the reaction mixture was stirred for the time shown in Table 2. After completion, the reaction mixture was filtered and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and solvent was removed in vacou. The crude product was subjected to silica gel

column chromatography using hexane:EtOAc (90:10) to yield the products **(2a, 2b, 2f, 2i, 2k)**.

4.1.2. The One-Pot Conversion of Chalcone Epoxides To 1,2,3-Triketones (3a-P) (Table 3)

A solution of chalcone epoxide (1 mmol) and *β*-CD (1 mmol) in H_2O/DMSO (1:1) (10 mL) were added LiBr (1.2 mmol) and the mixture was stirred at room temperature. As soon as the starting material disappeared (as monitored by TLC analysis), IBX (2.5 mmol) was introduced into the same pot and the reaction mixture was stirred for the time shown in Table 3. After completion, the reaction mixture was filtered and extracted with ethyl acetate. The crude product was subjected to silica gel column chromatography using hexane : EtOAc (85 : 15) to yield the products. The product obtained was heated at 100-120 ^{o}C for 6 h under reduced pressure in nitrogen atmosphere to give VTCs.

4.2. Characterization

4.2.1.1. 3-Bromo-2-Hydroxy-1,3-Diphenylpropan-1-One (2a)

Light yellow solid, mp 90-92 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.66-7.63 (m, 1H), 7.54-7.50 (m, 4H), 7.37-7.29 (m, 3H), 5.39 (d, *J* = 2 Hz, 1H), 5.24 (d, *J* = 2H, 1H), 3.99 (s, 1H, D_2O exchangeable).^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ 199.3, 139.0, 135.4, 133.7, 132.5, 131.2, 129.9, 129.4, 127.9, 75.3, 56.4. IR (KBr, cm^{-1}): 3425, 2948, 1640, 1599, 1582. HRMS (ESIMS) for $C_{15}H_{13}BrNaO_2(M+Na)^+$ Anal. calcd. 326.9991; found 326.9989.

1,3-Diphenylpropane-1,2,3-Trione (3a)

Light yellow solid, mp 67-73 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.08 (dd, *J* = 2, 8.4 Hz, 4H), 7.71-(t, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 4H).^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ192.2, 179.8, 135.7, 132.4, 130.3, 129.3. IR (KBr, cm^{-1}): 1695, 1645. HRMS (ESIMS) for $C_{15}H_{10}NaO_3$ $(M+Na)^+$ Anal. calcd. 261.0522; found 261.0520.

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Verma, N.; Zubair, S.; Faisal, S. M.; Kazmi, S.; Chakraborty, S.; Owais, M.; Ahmed, N., *J. Heterocyclic Chem*., **2017,** doi: 10.1002/jhet.2812.

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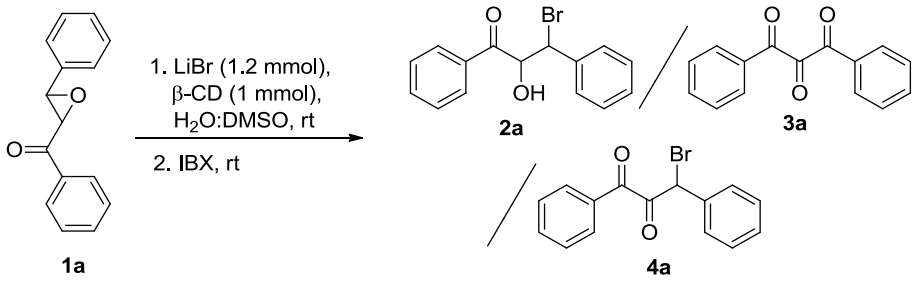
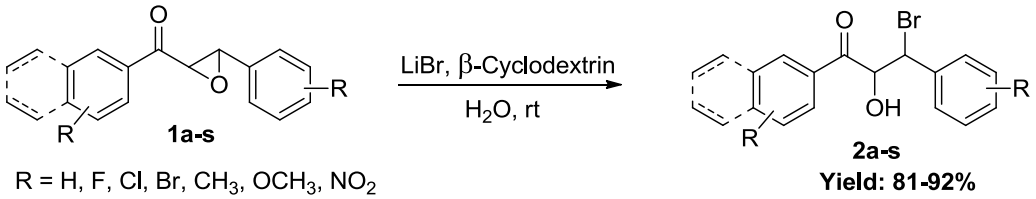
Table 1. Optimization of reaction conditions.[b]



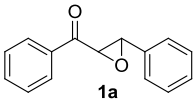
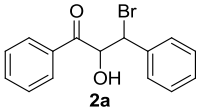
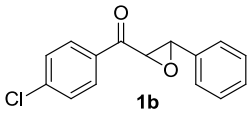
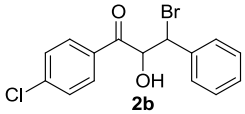
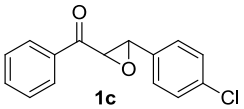
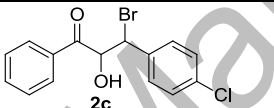
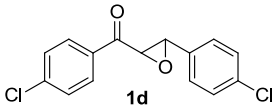
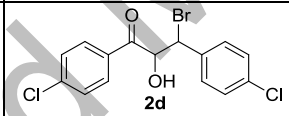
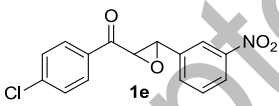
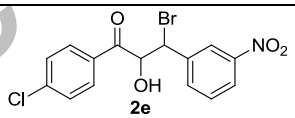
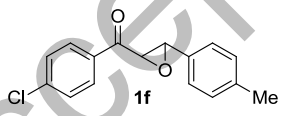
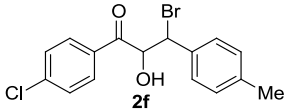
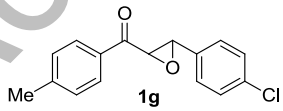
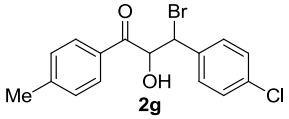
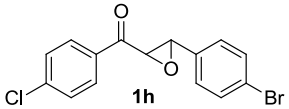
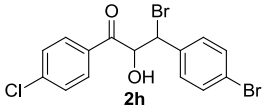
Entry	H_2O:DMSO (v/v)	IBX (eq.)	Time (h)	Yield (%)[c]		
				2a	**3a**	**4a**
1	0:100	0	15	15	-	-
2	100:0	0	8	71	-	-
3	0:100	2.5	15	-	15	-
4	100:0	2.5	15	--	-	79
5	3:1	2.5	18	-	60	-
6	2:1	2.5	18	-	71	-
7	**1:1**	**2.5**	**10**	**-**	**81**	**-**

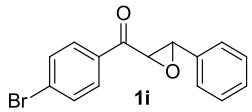
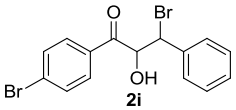
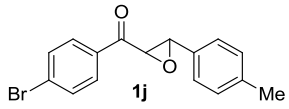
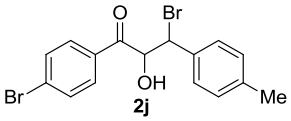
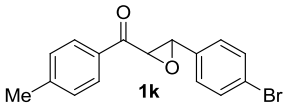
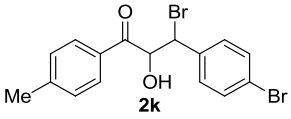
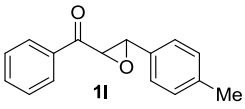
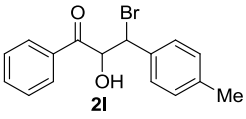
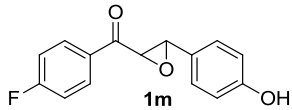
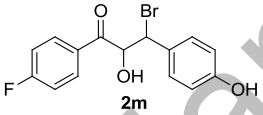
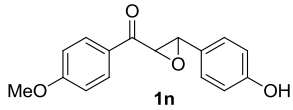
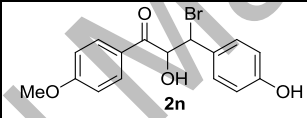
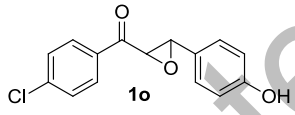
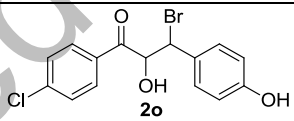
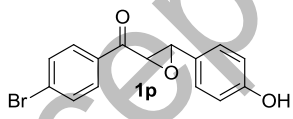
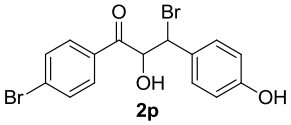
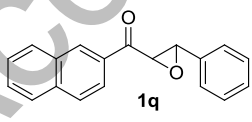
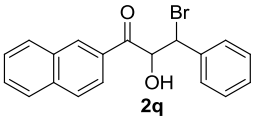
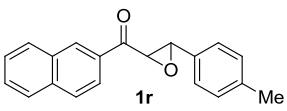
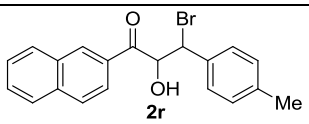
[b]Reaction was carried out on 1 mmol scale; [c]isolated yield.

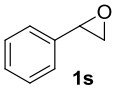
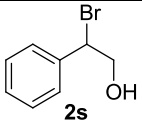
Table 2. Conversion of chalcone epoxides to bromohydrins.[a]



R = H, F, Cl, Br, CH_3, OCH_3, NO_2

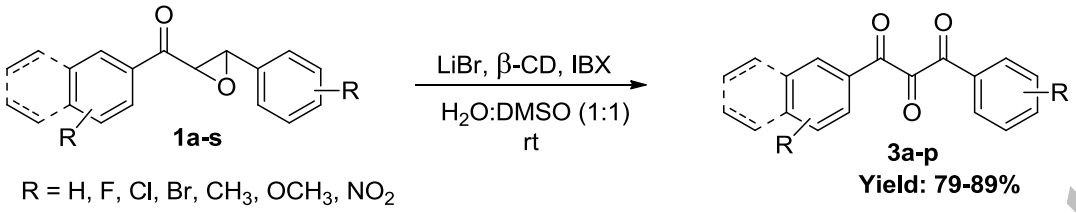
Entry	Chalcone epoxide	bromohydrin ketone (**2a-s**)	Time (h)	Yield (%)[b]
1			6	92
2			6	91
3			7	89
4			7	88
5			5.5	90
6			6.5	92
7			6	92
8			6	87

9	 **1i**	 **2i**	6	88
10	 **1j**	 **2j**	7	89
11	 **1k**	 **2k**	6	88
12	 **1l**	 **2l**	7	91
13	 **1m**	 **2m**	7.5	86
14	 **1n**	 **2n**	7.5	85
15	 **1o**	 **2o**	8	87
16	 **1p**	 **2p**	7.5	85
17	 **1q**	 **2q**	7	82
18	 **1r**	 **2r**	7	83

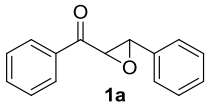
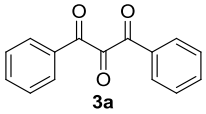
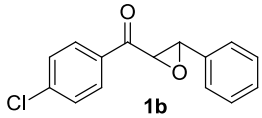
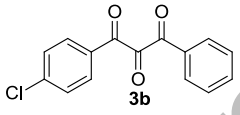
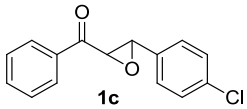
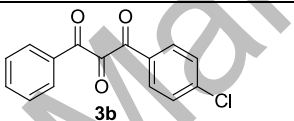
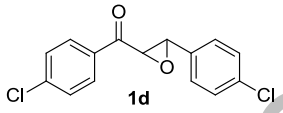
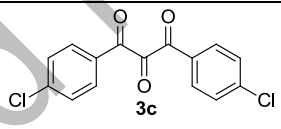
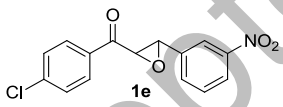
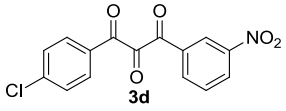
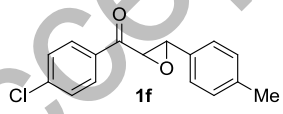
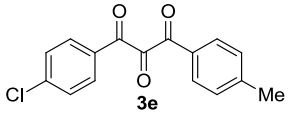
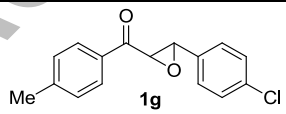
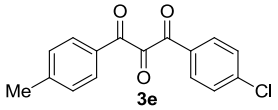
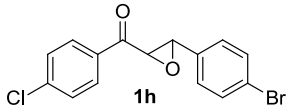
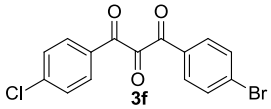
19	 1s	 2s	5	83

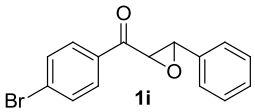
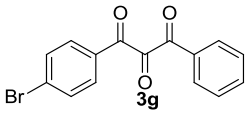
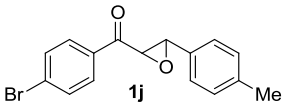
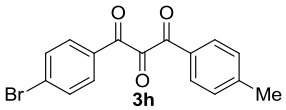
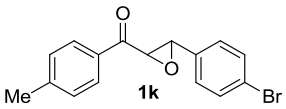
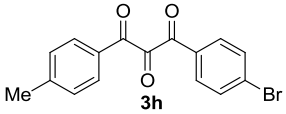
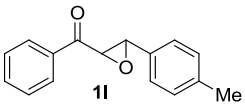
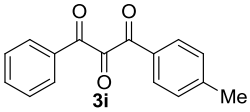
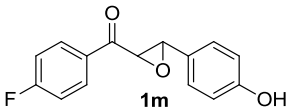
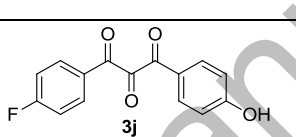
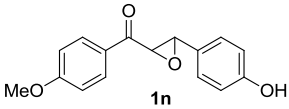
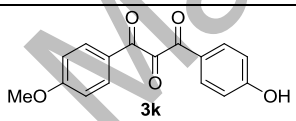
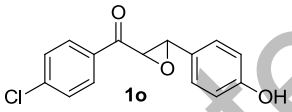
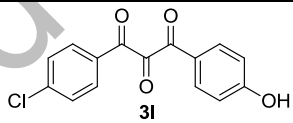
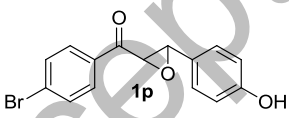
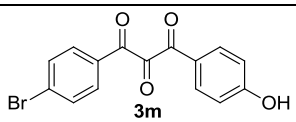
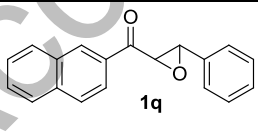
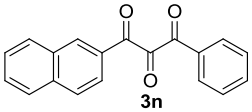
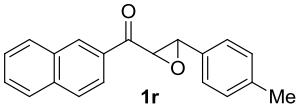
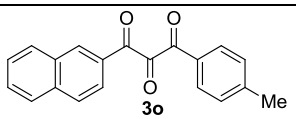
Reaction conditions: Chalcone epoxide (1 mmol), *β*-CD (1 mmol), LiBr (1.2 mmol), H_2O (10 mL). [b]GC Yield.

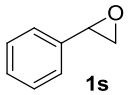
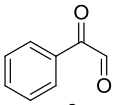
Table 3. Transformation of chalcone epoxides to 1,2,3- triketones.[a]



R = H, F, Cl, Br, CH_3, OCH_3, NO_2

Entry	Chalcone epoxide	Triketones (**3a-p**)	Time (h)	Yield (%)[b]
1			10	81
2			10	75
3			10	76
4			11	74
5			9.5	78
6			11	74
7			11	79
8			10	81

9	 **1i**	 **3g**	10	78
10	 **1j**	 **3h**	11	79
11	 **1k**	 **3h**	11	77
12	 **1l**	 **3i**	11	80
13	 **1m**	 **3j**	11	76
14	 **1n**	 **3k**	12	74
15	 **1o**	 **3l**	11	75
16	 **1p**	 **3m**	11	77
17	 **1q**	 **3n**	10	75
18	 **1r**	 **3o**	11	72

19	 1s	 3p	8	76

[a]Reaction conditions: Chalcone epoxide (1 mmol), *β*-CD (1 mmol), LiBr (1.2 mmol), IBX (2.5 mmol), H_2O:DMSO (10 mL). [b]isolated yield.

Scheme 1. Mechanism for the oxidation of chalcone epoxides to tricarbonyl compounds.

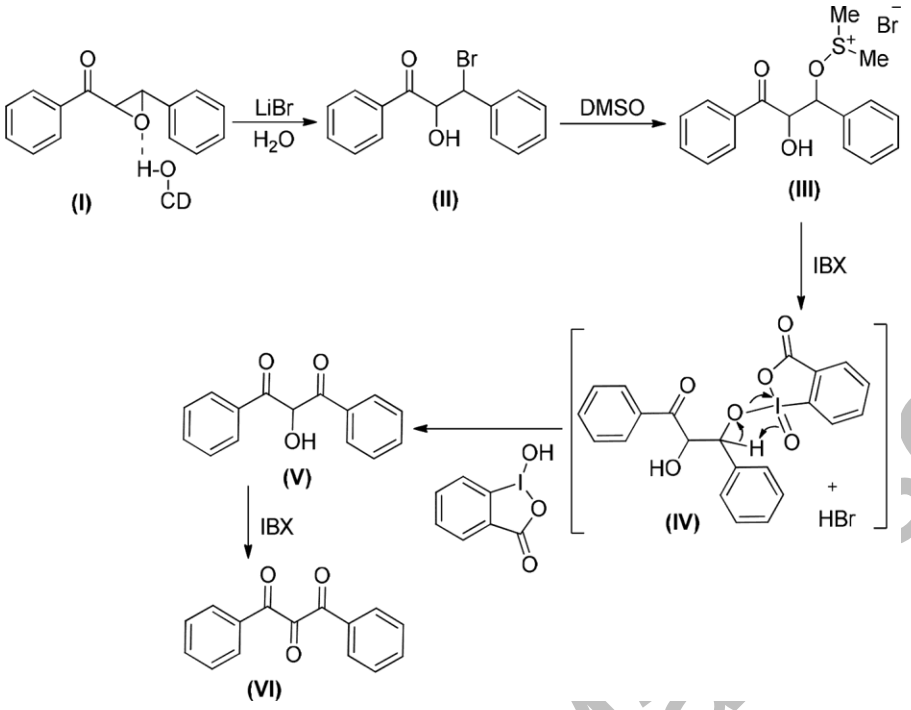


Figure 1. Mechanistic Rationale of LiBr/*β*-CD induced transformation of chalcone epoxide to bromohydrin