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Retro-Corey-Chaykovsky Epoxidation: Converting Geminal Disubstituted Epoxides to Ketones

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Corey-Chaykovsky epoxidation has been widely applied in the conversion of aldehydes and ketones to epoxides with sulfonium and sulfoxonium ylides. The reverse transformation is realized for conversion of geminal disubstituted epoxides to ketones in the presence of DABCO in refluxing mesitylene. The method is a weak basic transformation from epoxides to ketones with loss of a methylene group and can be applied as an alternative strategy of the acid-catalyzed Meinwald rearrangement or oxidation for conversion of epoxides to carbonyl compounds.

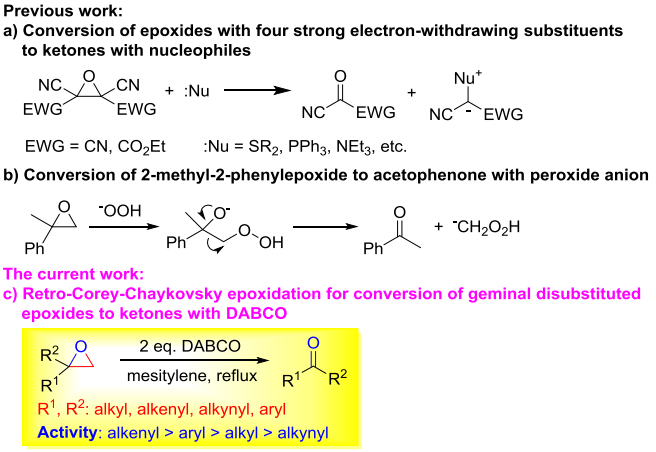
Keywords: DABCO • epoxide • ketone • retro-epoxidation • ylide

Introduction

In 1962 and 1965, Corey and Chaykovsky prepared epoxides from aldehydes and ketones with dimethylsulfoxonium and dimethylsulfonium methylides, generated from trimethylsulfoxonium and trimethylsulfonium halides, respectively, in the presence of sodium hydride under nitrogen at room temperature through deprotonation.[1,2] Both dimethylsulfoxonium and dimethylsulfonium methylides are sulfur ylides. The preparation of epoxides from aldehydes and ketones with sulfur ylides is known as the Corey-Chaykovsky epoxidation.[3] Since that time, the Corey-Chaykovsky epoxidation has been widely applied in the synthesis of epoxides, aziridines, and cyclopropanation, even their optically active analogues.[4,5] Recently, ammonium ylide-mediated epoxidation reactions of aldehydes have been developed as well.[6-9] On the other hand, earlier than the Corey-Chaykovsky epoxidation, the reverse reaction was also reported, but has paid less attention to date.[10-13] The reaction of tetracyanoepoxide and some nucleophiles without active hydrogen atom, including triphenylphosphine, tertiary amines, pyridines, isoquinoline, and dialkyl sulfides, generated carbonyl cyanide (a ketone with two strong electron-withdrawing cyano groups) and the corresponding ylides (Scheme 1, a). Subsequently, diethyl 2,3-dicyanooxirane-2,3-dicarboxylate was treated with diheptyl sulfide to generate ethyl 2-cyano-2-oxoacetate (a ketone with strong electron-withdrawing cyano and carboxylate groups) as a dienophile and enophile for the in situ use in cycloadditions by loss of a sulfur ylide (Scheme 1, a).[14] Besides the reactions of epoxides with four electron-withdrawing substituents and nucleophiles without active hydrogen atom, only one example of the retro reaction of Corey-Chaykovsky epoxidation of 2-methyl-2-phenylepoxide and hydrogen peroxide in the presence potassium hydroxide has been exploited (Scheme 1, b).

Alternatively, the conversion of epoxides to the carbonyl compounds (aldehydes and ketones) was realized previously through the oxidative C-C cleavage of epoxides with some oxygen-transfer reagents, such as ozone, *meta*-chloroperbenzoic acid, pyridinium chlorochromate, and ozone or pyridine *N*-oxide under photoirradiation. However, the conversion yields were generally from low to moderate.[15,16]

When we investigated nucleophilic organic base DABCO-mediated Meinwald rearrangement of terminal epoxides into methyl ketones, monosubstituted epoxides rearranged into methyl ketones.[17] However, we observed that DABCO could promote geminal disubstituted epoxides to convert to ketones. Ammonium ylides have been applied in the epoxidation of aldehydes.[6-9] Our observation could be considered as retro-Corey-Chaykovsky epoxidation. It should be a useful reaction for conversion of epoxides into ketones under non-oxidative mild basic conditions. We previously studied the scope and limitation of the Corey-Chaykovsky epoxidation.[18] We, herein, present a systematic investigation on the retro-Corey-Chaykovsky epoxidation for conversion of epoxides into ketones and its scope and limitation (Scheme 1, c).



Scheme 1. Retro-Corey-Chaykovsky Epoxidation for Conversion of Epoxides to Ketones.

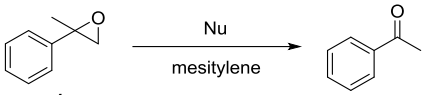
Results and Discussion

At first, 2-methyl-2-phenylepoxide (**1a**) was selected as the model substrate to optimize reaction conditions (Table 1). Initially, epoxide **1a** was stirred in mesitylene in the presence of 2 equivalents of DABCO at 130 °C for 48 h. No reaction occurred (Table 1, entry 1). The product acetophenone (**2a**) was obtained in 22% yield when the reaction temperature was raised to 165 °C (Table 1, entry 2). The yield was improved to 31% when the reaction time was prolonged to 60 h (Table 1, entry 3). Other active hydrogen-free nucleophiles were also tested as the nucleophiles because nucleophiles with active hydrogen atom would undergo nucleophilic ring-opening reaction. Triphenylphosphine gave acetophenone in only 7% yield (Table 1, entry 4). Both diphenyl sulfide and thioanisole were not efficient nucleophiles for the reaction (Table 1, entries 5 and 6). Several representative acidic additives, neutral water (weak protonic acid), protonic acid TsOH, and Lewis acid $CuCl_2 \cdot H_2O$, were attempted, resulted in obvious decrease of the yield (Table 1, entries 7–9). Microwave acceleration was not observed, either, when the reaction was conducted under microwave

10.1002/hlca.201900164

irradiation at 165 °C for 1 h (Table 1, entry 10), although microwave irradiation assisted some epoxide-participated organic reactions.[19-21] Although the conversion yield of epoxide **1a** to acetophenone (**2a**) was not satisfactory, to investigate the scope and limitation of the conversion, other representative geminal disubstituted epoxides **1** were further evaluated under the conditions of 2 equivalents of DABCO in mesitylene at 165 °C for 48 or 60 h (Table 2). First, different 2-aryl-2-methylepoxides **1a-1d** were examined, affording the corresponding acetophenones in low yields of 13-31% (Table 1, entries 1–4). Several 2-aryl-2-alkenylepoxides **1e-1h** were tested, giving the desired α,β-unsaturated ketones **2e-2h** in satisfactory yields of 40-61% (Table 2, entries 5–8). 2-Aryl-2-alkynylepoxide 2-phenyl-2-phenylethynylepoxide (**1i**) was also tried, producing a trace amount of 1,3-diphenylprop-2-yn-1-one (**2i**) (Table 2, entry 9). For 2,2-diarylepoxide, 2,2-diphenylepoxide (**1j**) yielded benzophenone (**2j**) in only 21% yield (Table 2, entry 10).

Table 1. Optimization for the Conversion of 2-Methyl-2-Phenylepoxide to Acetophenone.[a]

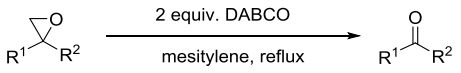


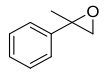
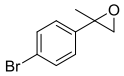
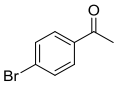
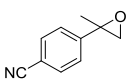
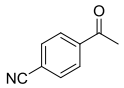
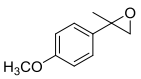
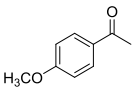
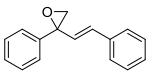
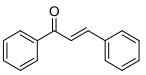
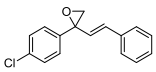
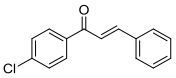
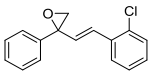
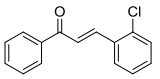
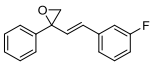
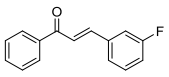
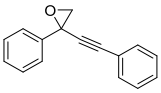
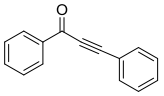
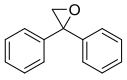
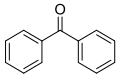
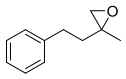
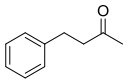
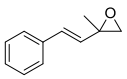
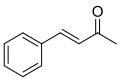
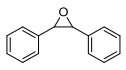
1a **2a**

Entry	Nu	Additive (eq.)	Temp. (°C)	Time (h)	Yield[b] (%)
1	DABCO		130	48	0
2	DABCO		165	48	22
3	DABCO		165	60	31
4	PPh_3		165	48	7
5	Ph_2S		165	48	0
6	PhSMe		165	48	0
7	DABCO	H_2O (4)	165	48	9
8	DABCO	$TsOH{\cdot}H_2O$ (0.1)	165	48	Trace[c]
9	DABCO	$CuCl_2{\cdot}2H_2O$ (0.1)	165	48	4
10	DABCO		165	1	0[d]

[a] All the reactions were performed on a 0.5 mmol scale of **1a** and 1.0 mmol of nucleophile (Nu). [b] Yields of the isolated product **2a**. [c] 2-Phenylpropanal was obtained in 30% yield. [d] Microwave irradiation heating at 165 °C for 1 h.

Table 2. DABCO-promoted conversion of geminal disubstituted epoxides to methyl ketones[a]



Entry	Substrate 1	Time (h)	Product 2	Yield (%)[a]
1	 **1a**	60	 **2a**	31
2	 **1b**	40	 **2b**	28
3	 **1c**	48	 **2c**	21
4	 **1d**	48	 **2d**	13
5	 **1e**	48	 **2e**	59
6	 **1f**	48	 **2f**	61
7	 **1g**	48	 **2g**	47
8	 **1h**	48	 **2h**	40
9	 **1i**	48	 **2i**	trace
10	 **1j**	48	 **2j**	21
11	 **1k**	48	 **2k**	15
12	 **1l**	60	 **2l**	7
13	 **1m**	60	-	NR
14	 **1n**	48	-	NR

[a] All the reactions were performed on a 0.5 mmol scale of epoxide **1** and DABCO (1 mmol) in 2 mL of mesitylene were stirred at 165 °C, yields are isolated yields.

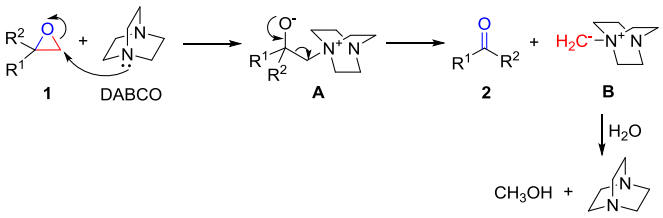
Next, disubstituted alkylepoxides **1k** and **1l** were examined as well. 2-Methyl-2-(2-phenylethyl)epoxide (**1k**) was converted to 4-phenylbutan-2-

one (**2k**) in only 15% yield under the same conditions (Table 2, entry 11). Similarly, 2-methyl-2-styrylepoxide (**1l**) gave a low yield (7%) of 4-phenylbut-3-en-2-one (**2l**) (Table 2, entry 12).

Finally, two representative vicinal disubstituted epoxides, 2,3-diarylepoxide 2,3-diphenylepoxide (**1o**) and 2,3-diaklylepoxide cyclohexene oxide (**1p**) were checked. However, for both of them, no reaction occurred possibly due to their steric hindrance and less electrophilicity (Table 2, entries 13 and 14). Bulky tetrasubstituted epoxides with four strong electron-withdrawing substituents underwent the conversion smoothly due to their strong electrophilicities.[10-12] However, bulky vicinal 2,3-dialkyl and diarylepoxides possessed only weak electrophilicity, unfavorable in the nucleophilic attack by DABCO.

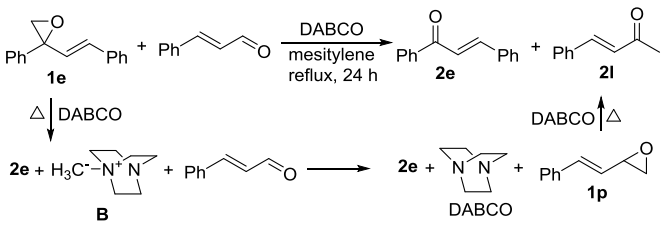
The results indicated that only 2-aryl-2-styrylepoxides favored retro-Corey-Chaykovsky epoxidation with DABCO as a nucleophile in refluxing mesitylene, affording the corresponding ketones in satisfactory yields. Other geminal disubstituted epoxides showed low efficiency in the conversion.

After obtaining the above information, we proposed the following mechanism, DABCO as a nucleophile first nucleophilically attacks the less substituted carbon atom of geminal disubstituted epoxides **1** to generate zwitterionic intermediates **A**, which undergo an elimination of DABCO ammonium methylide **B** to give rise to methyl ketones **2** (Scheme 2). During the ring-opening reaction, the regioselectivity follows the general regioselectivity in the nucleophilic ring-opening of the three-membered heterocycles.[22-27] The ammonium methylide **B** decomposes into DABCO and methanol through the reaction with water during workup.



Scheme 2. Proposed Mechanism for the Retro-Corey-Chaykovsky Epoxidation.

On the basis of DFT calculational results,[6,8,9] the formation of betaine intermediates from aldehydes and ammonium ylides is reversible and DABCO is not a good leaving group. In the current cases, when the intermediates **A** generate, the ring closure for formation of epoxides **1** is unfavorableby by loss of DABCO from intermediate **A**, resulting in the occurence of retro-Corey-Chaykovsky epoxidation to give rise to ketones **2** and DABCO ammonium methylide **B**. Ketones show poor reactivity in the ammonium ylide-mediated epoxidation. Thus, ketones **2** and DABCO ammonium methylide **B** cannot undergo Corey-Chaykovsky epoxidation.



Scheme 3. Verification of the Generation of DABCO Ammonium Methylide **B**.

To verify the generation of the DABCO ammonium methylide **B**, the experiment on the ammonium methylide **B** transfer was conducted. A solution of equivalent amounts of 2-phenyl-2-styrylepoxide (**1e**) and cinnamaldehyde in mesitylene was refluxed in the presence of 2 equivalents of DABCO for 24 h. The resulting solution was subjected GC-MS analysis, revealing that chalcone (**2e**) and 4-phenylbut-3-en-2-one (**2l**) were observed and verified by comparison with the authentic samples (Scheme 3). The results indicated that the retro-Corey-Chaykovsky epoxidation of epoxide **1e** and DABCO generated chalcone (**2e**) and the DABCO ammonium ylide **B**, which reacted with less steric cinnamldehyde to yield styrylepoxide (**1p**) and DABCO. They further underwent the DABCO-mediated Meinwald rearrangement under heating conditions to give final product 4-phenylbut-3-en-2-one (**2l**) as previously reported by us.[17] The designed experimental results perfectly verified the generation of the DABCO ammonium methylide **B** in the reaction, further supporting our proposed mechanism for the retro-Corey-Chaykovsky epoxidation.

Conclusions

In summary, we developed a direct and simple strategy to realize retro-Corey-Chaykovsky epoxidation for the conversion of geminal disubstituted epoxides to ketones. Although the strategy just shows a limited substrate scope with low to moderate yields, the method is only suitable for geminal disubstituted epoxides, especially, 2-aryl-2-alkenylepoxides, it can serve as an important alternative to the acid-catalyzed or nucleophile-participated Meinwald rearrangements or the oxidative C-C cleavage method for conversion of epoxides to ketones. The method may provide an idea and beginning for other organic chemists to improve this transformation and finally to realize it efficiently under mild conditions in the future.

Experimental Section

Instrumentation and Chemicals

Unless otherwise noted, all materials were purchased from commercial suppliers. DCE was refluxed over CaH_2, and freshly distilled prior to use. Flash column chromatography was performed using silica gel (normal phase, 200–300 mesh) from Branch of Qingdao Haiyang Chemical. Petroleum ether (PE) used for column chromatography is 60–90 °C fraction, and the removal of residue solvent was accomplished under rotovap. Reactions were monitored by thin-layer chromatography (TLC) on silica gel GF254 coated 0.2 mm plates from Institute of Yantai Chemical Industry. The plates were visualized under UV light, as well as other TLC stains (10% phosphomolybdic acid in ethanol; 1% potassium permanganate in water; 10 g of iodine absorbed on 30 g of silica gel). ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$ with TMS as an internal standard, and the chemical shifts (δ) are reported in parts per million (ppm). All coupling constants (J) in ^{1}HNMR are absolute values given in hertz (Hz) with peaks labeled as single (s), broad singlet (brs), doublet (d), triplet (t), quartet (q), and multiplet (m). The IR spectra (KBr pellets, ν [cm^{-1}]) were taken on a Nicolet 5700 FTIR spectrometer. HRMS measurements were carried out on an Agilent LC/MSD TOF mass spectrometer. Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected.

General Procedure for the Preparation of Epoxides **1**

Epoxides **1a**-**1l** were prepared from trimethylsulfonium iodide and the corresponding ketones using Johnson-Corey-Chaykovsky reaction.[17] Sodium hydride (300 mg, 7.5 mmol, 60% mineral oil dispersion) was washed with petroleum ether (3 × 5 mL). The residual petroleum ether was removed under vacuum. Under atmosphere of nitrogen, dry THF (15 mL) and dry DMSO (15 mL) were added and the reaction mixture was cooled in an ice bath. A solution of trimethylsulfonium iodide (1.22 g, 6 mmol) in DMSO (4 mL) was added. After addition, a ketone (5 mmol) was added in one portion. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for an additional 12 h. The reaction mixture was slowly quenched with a mixture of water and ice (20 mL) and extracted with methylene chloride (3 × 10 mL). The combined organic extracts were washed with brine (2 × 30 mL), dried over sodium sulfate, and filtered. The reaction mixture was directly subjected to flash column chromatography with ethyl acetate/petroleum ether (1:25, *v*/*v*) to give epoxide **1**.

2,3-Diphenyloxirane (**1m**) was prepared from 1,2-diphenylethene using the MCPBA epoxidation reaction.[17] To a solution of 1,2-diphenylethene (900 mg, 5.0 mmol) in DCM (20 mL) in a 100 mL flask was added MCPBA (1.5 g, 7.5 mmol, 85%) at 0 °C. The reaction mixture was allowed to stir at room temperature overnight. The solution was then washed with $NaHCO_3$ aq (20 mL) and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified on silica gel column chromatography with a mixture of petroleum ether/EtOAc (20:1, v/v) to afford the desired epoxide **1m**.

Epoxide **1n** is commercial available. Epoxides **1a-1e** and **1i-1m** are known compounds.

2-Methyl-2-phenyloxirane (1a).[18] Colorless liquid. 482 mg, yield 72%. R_f = 0.64, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.11 (m, 5H), 2.89 (d, J = 5.4 Hz, 1H), 2.72 (d, J = 5.4 Hz, 1H), 1.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 128.3, 127.4, 125.3, 64.9, 57.0, 21.8.

2-(4-Bromophenyl)-2-methyloxirane (1b).[28,29] Colorless oil. 0.934 g, yield 88%. R_f = 0.71, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 2.95 (d, J = 5.4 Hz, 1H), 2.73 (d, J = 5.3 Hz, 1H), 1.68 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.3, 131.4, 127.1, 121.4, 56.9, 56.3, 21.5.

4-(2-Methyloxiran-2-yl)benzonitrile (**1c**).[30] Colorless liquid. 490 mg, yield 62%. R_f = 0.50, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 3.03 (d, J = 5.3 Hz, 1H), 2.76 (d, J = 5.3 Hz, 1H), 1.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 132.1, 126.0, 118.5, 111.2, 57.0, 56.1, 21.0.

2-(4-Methoxyphenyl)-2-methyloxirane (**1d**).[31] Colorless liquid. 400 mg, yield 49%. R_f = 0.70, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 3.78 (s, 3H), 2.94 (d, J = 5.4 Hz, 1H), 2.78 (d, J = 5.3 Hz, 1H), 1.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 133.2, 126.5, 113.6, 56.9, 56.4, 55.2, 21.9.

2-Phenyl-2-styryloxirane (1e).[32] Colorless liquid. 1.6 g, yield 72%. R_f = 0.75, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.43 (m, 2H), 7.43–7.21 (m, 8H), 6.62–6.47 (m, 1H), 6.45–6.32 (m, 1H), 3.21 (dd, J = 5.5, 2.0 Hz, 1H), 3.12 (dd, J = 5.5, 2.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 136.2, 133.8, 128.7, 128.6, 128.3, 128.0, 127.9, 127.1, 126.5, 60.4, 57.2.

(*E*)-2-(4-Chlorophenyl)-2-styryloxirane (1f). Colorless oil. 152 mg, yield 20%. R_f = 0.80, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.26 (m, 9H), 6.53 (d, J = 16.0 Hz, 1H), 6.33 (d, J = 16.0 Hz, 1H), 3.21 (d, J = 5.6 Hz, 1H), 3.07 (d, J = 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 135.9, 134.2, 128.9, 128.6, 128.6, 128.2, 128.1, 127.2, 126.6, 126.5, 59.9, 57.2. HRMS (ESI) *m/z*: calcd. for $C_{16}H_{14}ClO^+[M+H]^+$: 257.0728; found: 257.0728.

(*E*)-2-(2-Chlorostyryl)-2-phenyloxirane (**1g**). Yellow oil. 703 mg, yield 92%. R_f = 0.65, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.5 Hz, 1H), 7.48 (dd, J = 7.1, 1.2 Hz, 2H), 7.42 – 7.30 (m, 4H), 7.24 – 7.12 (m, 2H), 6.97 (d, J = 16.0 Hz, 1H), 6.38 (d, J = 16.0 Hz, 1H), 3.23 (d, J = 5.6 Hz, 1H), 3.13 (d, J = 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 134.5, 133.2, 131.5, 130.1, 129.7, 129.0, 128.4, 128.0, 127.0, 126.9, 126.8, 60.3, 57.3. HRMS (ESI) *m/z*: calcd. for $C_{16}H_{14}ClO^+[M+H]^+$: 257.0728; found: 257.0726.

(*E*)-2-(3-Fluorostyryl)-2-phenyloxirane (**1h**). Colorless liquid. 697 mg, yield 97%. R_f = 0.70, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.19 (m, 5H), 7.17–7.10 (m, 1H), 6.96 (ddd, J = 10.2, 9.2, 4.7 Hz, 2H), 6.82 (td, J = 8.3, 2.0 Hz, 1H), 6.41 (d, J = 16.0 Hz, 1H), 6.29 (d, J = 16.0 Hz, 1H), 3.08 (d, J = 5.6 Hz, 1H), 3.01 (d, J = 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (d, J = 245.6 Hz), 138.5 (d, J = 7.7 Hz), 137.9, 132.5 (d, J = 1.9 Hz), 130.0 (d, J = 8.4 Hz), 128.4, 128.0, 127.1, 122.4 (d, J = 2.2 Hz), 114.8 (d, J = 21.4 Hz), 112.9 (d, J = 21.9 Hz), 60.2, 57.2. ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.23.HRMS (ESI) m/z: calcd. for $C_{16}H_{14}FO^+[M+H]^+$: 241.1023; found: 241.1021.

2-Phenyl-2-(phenylethynyl)oxirane (**1i**).[33] Yellow oil. 500 mg, yield 45%. R_f = 0.90, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.54 (m, 2H), 7.51 (ddd, J = 4.9, 1.9, 0.6 Hz, 2H), 7.38 (t, J = 7.3 Hz, 2H), 7.35–7.28 (m, 4H), 3.52 (d, J = 6.1 Hz, 1H), 3.10 (d, J = 6.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.2, 132.0, 131.8, 128.8, 128.4, 128.4, 128.3, 125.6, 121.9, 86.6, 84.3, 59.4, 51.4.

2,2-Diphenyloxirane (1j).[18] White crystals. m.p. 54-56 °C. (Lit.[18] M.p. 55–56 °C). 1.0 g, yield 51%. R_f = 0.75, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.27 (m, 10H), 3.27 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 129.2, 129.0, 128.3, 128.0, 127.5, 61.84, 56.9.

2-Methyl-2-phenethyloxirane (1k).[28,29] Colorless liquid. 240 mg, yield 30%. R_f = 0.85, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, J = 7.8, 7.3 Hz, 2H), 7.19 (d, J = 7.0 Hz, 1H), 7.18 (d, J = 7.7 Hz, 2H), 2.74–2.68 (m, 2H), 2.58 (dd, J = 11.0, 4.9 Hz, 2H), 1.97–1.77 (m, 2H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 128.4, 128.2, 125.9, 56.6, 53.9, 38.5, 31.4, 21.0.

(*E*)-2-Methyl-2-styryloxirane (1l).[34] Colorless liquid.480 mg, 60%. R_f = 0.85, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.14 (m, 5H), 6.82–6.46 (m, 1H), 5.94 (d, J = 16.2 Hz, 1H), 2.83 (d, J = 5.2 Hz, 1H), 2.77 (d, J = 5.2 Hz, 1H), 1.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.3, 131.6, 130.6, 128.6, 127.8, 126.4, 67.9, 56.2, 19.8.

2,3-Diphenyloxirane (1m).[35] Colorless crystals. M. p. 68–70 °C. (Lit.[36] M.p. 67–69 °C). 0.945 g, yield 48%. R_f = 0.82, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.14 (m, 10H), 3.87 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 128.6, 128.3, 125.5, 62.8.

*General procedure for the retro-Corey-Chaykovsky epoxidation of epoxides **1***

Epoxide **1** (0.5 mmol) was dissolved in 2 mL of mesitylene in a 10 mL reaction tube. After DABCO (112 mg, 1.0 mmol) was added at room temperature, the reaction mixture was heated at 165 °C for 48 h. After cooling to room temperature, the reaction mixture was directly subjected to flash column chromatography with ethyl acetate/petroleum ether (1:50, *v/v*) to afford product **2**. All ketones are known products.

Phenylethan-1-one (2a).[37] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as colorless oil, 19 mg, 31% yield R_f = 0.27, 5% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.92 (m, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.47 (dd, J = 7.6 7.6, Hz, 2H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1, 137.0, 133.0, 128.5, 128.2, 26.5.

1-(4-Bromophenyl)ethan-1-one (2b).[38] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as white solid, 28 mg, 28% yield. M.p. 57–58 °C. (Lit.[39] M.p. 52–53 °C). R_f = 0.30, 6.67% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.5 Hz, 2H), 7.61 (d, J = 8.5 Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 135.8, 131.9, 129.8, 128.3, 26.5.

4-Acetylbenzonitrile (2c).[40] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as white solid. 15 mg, 21% yield. M.p. 60–63 °C. (Lit.[41] M.p. 59–60 °C). R_f = 0.14, 10% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 139.8, 132.4, 128.6, 117.8, 116.3, 26.7.

1-(4-Methoxyphenyl)ethan-1-one (2d).[42] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as colorless oil, 10 mg, 13% R_f = 0.18, 6.67% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 163.5, 130.6, 130.3, 113.7, 55.5, 26.3.

Chalcone (2e).[43] Purified by flash column chromatography (PE/EA 100:1, *v/v*) on silica gel to give the desired product as white crystals. m.p. 55–57 °C. (Lit.[44] M.p. 55–56 °C) 61 mg, 59% yield. R_f = 0.65, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 7.2, 1.4 Hz, 2H), 7.81 (d, J = 15.7 Hz, 1H), 7.64 (dd, J = 6.7, 2.8 Hz, 2H), 7.58–7.47 (m, 4H), 7.43–7.39 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 144.8, 138.2, 134.9, 132.7, 130.5, 128.9, 128.6, 128.5, 128.4, 122.1.

(*E*)-1-(4-Chlorophenyl)-3-phenylprop-2-en-1-one (2f).[45] Purified by flash column chromatography (PE/EA 100:1, *v/v*) on silica gel to give the desired product as light yellow solid m.p. 95–97 °C. (Lit.[45] M.p. 93–96 °C) 73mg, yield 61%. R_f = 0.7, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.97 (dd, J = 6.7, 1.9 Hz, 2H), 7.82 (d, J = 15.7 Hz, 1H), 7.70–7.61 (m, 2H), 7.51–7.46 (m, 3H), 7.45–7.42 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2, 145.4, 139.2, 136.5, 134.7, 130.7, 129.9, 129.0, 129.0, 128.5, 121.5

(*E*)-3-(2-Chlorophenyl)-1-phenylprop-2-en-1-one (2g).[43] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as light yellow solid. m.p. 49–51 °C. (Lit.[46] M.p. 52 °C) 57 mg, yield 47%. R_f = 0.55, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 15.8 Hz, 1H), 8.11–7.93 (m, 2H), 7.86–7.67 (m, 1H), 7.60 (dd, J = 7.3, 7.3 Hz, 1H), 7.51 (dd, J = 8.8, 6.3 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.37 – 7.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 140.7, 137.9, 135.5, 133.3, 132.9, 131.2, 130.3, 128.7, 128.6, 127.8, 127.1, 124.9.

(*E*)-3-(3-Fluorophenyl)-1-phenylprop-2-en-1-one (2h).[45] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as yellow solid. M.p. 86–90 °C. (Lit.[45] M.p. 87–92 °C) 46 mg, yield 40%. R_f = 0.6, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.2 Hz, 2H), 7.76 (d, J = 15.7 Hz, 1H), 7.61 (dd, J = 7.3, 7.3 Hz, 1H), 7.53 (d, J = 7.9 Hz, 2H), 7.52 (d, J = 15.7 Hz, 1H), 7.43–7.32 (m, 3H), 7.12 (ddd, J = 9.7, 5.2, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 167.2 (d, J = 267.1 Hz), 143.3, 137.9, 133.0, 130.5 (d, J = 8.3 Hz), 128.7, 128.5, 124.5, 123.2, 117.4 (d, J = 21.5 Hz), 114.5 (d, J = 21.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.46.

Benzophenone (2j).[47] Purified by flash column chromatography (PE/EA 100:1, *v/v*) on silica gel to give the desired product as white crystals. m.p. 48–51 °C. (Lit.[48] M.p. 48–49 °C). 19 mg, 21% yield. R_f = 0.78, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 7.0, 1.4 Hz, 4H), 7.58 (dddd, J = 7.4, 7.4, 1.4, 1.4 Hz, 2H), 7.47 (dd, J = 7.6, 7.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 137.6, 132.4, 130.0, 128.2.

4-Phenylbutan-2-one (2k).[49] Purified by flash column chromatography (PE/EA 100:1, *v/v*) on silica gel to give the desired product as colorless liquid. 11 mg, 15% yield. R_f = 0.80, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 7.20 (d, J = 6.8 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H), 2.76 (t, J = 7.5 Hz, 2H), 2.14 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 141.0, 128.5, 128.3, 126.1, 45.2, 30.1, 29.7.

(*E*)-4-Phenylbut-3-en-2-one (2l).[50] Purified by flash column chromatography (PE/EA 100:1, *v/v*) on silica gel to give the desired product as red-brown oil, 5 mg, 7% yield, 85% (0.5 mmol scale). R_f = 0.3, 5% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.47 (m, 3H), 7.42–7.35 (m, 3H), 6.71 (d, J = 16.3 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 143.4, 134.4, 130.5, 128.9, 128.2, 127.1, 27.5.

Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/MS-number.

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Author Contribution Statement

J. X. conceived the idea and designed the experiments. *S. L.* performed the experiments. *P. L.* participated the design of the experiments and discussion. *J. X.* wrote the manuscript with contributions and review from all authors.

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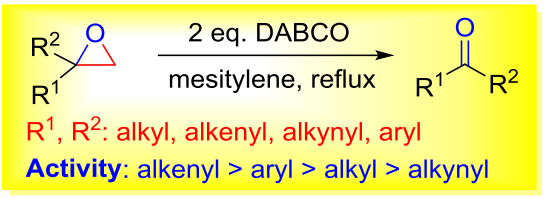

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The reverse transformation is realized for conversion of geminal disubstituted epoxides to ketones in the presence of DABCO in refluxing mesitylene.