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Dioxirane Epoxidation of α,β-Unsaturated Ketones

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The synthesis of epoxides **3a–r** is achieved in excellent yields by reaction of the α,β-unsaturated ketones **1a–c**, 4,4′-disubstituted (*E*)-chalcones **1d–o**, and 2′-hydroxy-4-substituted (*E*)-chalcones **1p–r** with isolated dimethyldioxirane (**2a**) (as acetone solution) and/or in situ generated ethyl(methyl)dioxirane (**2b**). This method constitutes a useful alternative to the Weitz-Scheffer epoxidation (alkaline H_2O_2) of such electron-poor substrates.

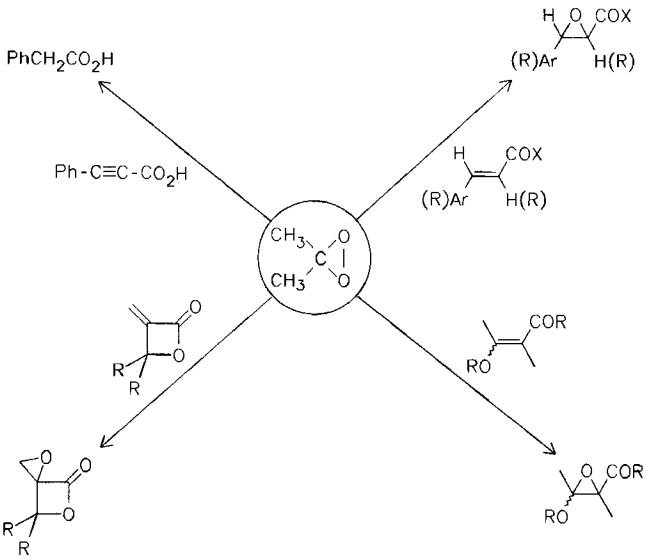
Chalcone epoxides are natural products which are commonly formed in plants[1] and exhibit important biological activity, e.g. they act as potent inhibitors of the cytosolic epoxide hydrolase[2]. The synthetic utility of such functionalized epoxides has been unquestionably demonstrated[3], a fact that underscores the need of new methods for the convenient and efficient preparation of these valuable "building blocks" in organic synthesis.

Two evident methodologies are either Sharpless epoxidation[4] of allylic alcohols and subsequent oxidation of the hydroxy functionality, or alternatively direct epoxidation of α,β-unsaturated ketones by alkaline hydrogen peroxide and its alkyl and silyl derivatives (Weitz-Scheffer reaction[5]). For base-sensitive functional groups, e.g. phenolic substituents, undesirable oxidations of the aromatic moiety may become prominent. The use of electrophilic oxidants such as peracids are frequently complicated by the facile Baeyer-Villiger rearrangement[6] of such electron-poor substrates. The base-catalyzed dehydrohalogenation of halohydrin may provide a useful entry into chalcone epoxides[7], but the preparation of the halohydrin precursors from the chalcones is not compatible with a number of functionalities.

Dimethyldioxirane (**2a**) is a selective and powerful oxygen transfer agent[8], that besides its high propensity to epoxidize electron-rich double bonds, has recently been shown to work well in its isolated form as acetone solution[9] with disubstituted α,β-unsaturated acids and esters[10], β-oxo enol ethers[11], and even the labile α-methylene-β-lactones[12] (Scheme 1). Previously, it was reported that the in situ generated dimethyldioxirane (**2a**) is effective for the epoxidation of cinnamic acids and esters[13], while the transformation of phenylpropiolic acid into phenylacetic acid was postulated to proceed through an oxirene intermediate[14].

In view of the convenience and efficiency of dimethyldioxirane (**2a**) as oxidant[8], we decided to test it in the direct conversion of α,β-unsaturated ketones into their epoxides. In this paper we describe our results obtained by using isolated dimethyldioxirane (**2a**) (as acetone solution) and our new in situ method, which utilizes ethyl(methyl)dioxirane (**2b**) prepared from 2-butanone and Caroate.

Scheme 1. Previous epoxidations of α,β-unsaturated carbonyl derivatives by dimethyldioxirane



Results and Discussion

The α,β-unsaturated ketones **1a–r** are transformed by isolated dimethyldioxirane (**2a**) (as acetone solution) into the corresponding epoxides **3a–r** (Scheme 2) in excellent yields. The results are given in Table 1 (Experimental), in which the time of epoxidation, the reaction temperature, and the yields are stated. The long reaction times (20–24 h), room temperature (ca. 20°C), the large excess of dimethyldioxirane (**2a**), and its addition in two portions are necessary for achieving total conversion of the α,β-unsaturated ketones **1** into the epoxides **3**, except for the 4-nitro derivative **1g**, for which in this time interval only 57% conversion is

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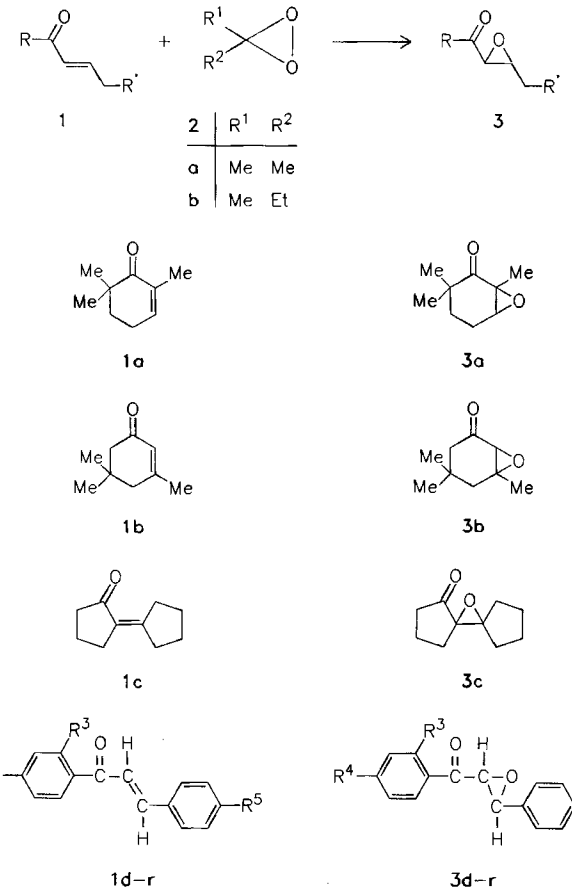
attained. Further batches of dioxirane and longer reaction times would be necessary to drive also this epoxidation to completion. Compared to the epoxidation by alkaline H_2O_2, which affords chalcone epoxide **3g** in only 43% yield[15], the usefulness of the dioxirane method is clearly evident for such sluggish reactions.

Scheme 2



2	R^1	R^2
a	Me	Me
b	Me	Et

1, 3	d	e	f	g	h	i	j	k
R^3	H	H	H	H	H	H	H	H
R^4	H	H	H	H	Me	OMe	Br	Me
R^5	H	Me	OMe	NO_2	H	H	H	Me

1, 3	l	m	n	o	p	q	r
R^3	H	H	H	H	OH	OH	OH
R^4	OMe	Me	OMe	Br	H	H	H
R^5	Me	OMe	OMe	OMe	H	Me	OMe

The most significant advantage of the dioxirane method is demonstrated for the 2′-hydroxy-substituted chalcones **1p–r**, which are converted quantitatively into the corresponding epoxides **3p–r** (Table 1, Experimental). Previous attempts to perform such epoxidations with, for example, alkaline H_2O_2[16], SeO_2[16], or $KMnO_4$[17] gave the respective flavonoids, while *m*-CPBA in refluxing $CHCl_3$ afforded only 20% yield of the desired epoxide[18]; these difficulties were overcome by protection of the 2′-hydroxy substituent with the acid-labile methoxymethyl group, followed by treatment with alkaline H_2O_2[19]. Such laborious protection methodology is obviated for the isolated dimethyldioxirane (**2a**), because the latter operates under strictly neutral conditions in the absence of bases.

Despite these advantages of the isolated dimethyldioxirane (**2a**), a large excess (at least threefold) must be employed to achieve complete epoxidation of electron-poor substrates such as α,β-unsaturated ketones **1** investigated herein. Thus, typically ca. 15 mmol of isolated dimethyldioxirane (**2a**) is required for the epoxidation of 4.7–7.0 mmol of substrate; however, as much as 500 mmol of Caroate is initially needed for the preparation of the ca. 15 mmol isolated dimethyldioxirane (**2a**). Although acetone and Caroate are inexpensive and the apparatus and procedure (Experimental) are simple and convenient, the isolated dimethyldioxirane oxidations are only practical for small-scale (up to 3 mmol) laboratory applications. Clearly, for larger scale operations the in situ method is preferred. For this purpose we developed a simplified in situ method, in which 2-butanone, also a common industrial solvent, is used instead of acetone.

In the usual in situ procedure[14] a saturated aqueous solution of Caroate is added to a well stirred, two-phase mixture, that consists of the substrate, acetone, CH_2Cl_2, or benzene as cosolvents, and a phase transfer catalyst (crown ether, tetraalkylammonium salts) under strictly buffered (pH = 7.3–7.5) conditions. Since 2-butanone is moderately soluble in water (ca. 120 g in 1000 ml), such 2-butanone/water mixtures provide directly the two-phase medium, and CH_2Cl_2 or benzene are only necessary as cosolvents when the solubility of the substrate requires it. Furthermore, in the 2-butanone/water medium no phase transfer catalyst is necessary.

By using the above procedures, a number of the α,β-unsaturated ketones **1** are converted by the in situ method into the corresponding epoxides **3** (Scheme 2) in excellent yields. Also in this general epoxidation procedure appropriate buffering keeps the pH at 7.3–7.5. In the case of (*E*)-4′-bromochalcone (**1j**) solubility problems in 2-butanone are encountered. By using CH_2Cl_2 as cosolvent and tetra-*n*-butylammonium hydrogen sulfate as phase transfer catalyst, this problem can be circumvented, and epoxide **3j** is isolated in 89% yield.

The only problematic case of the ones run with the in situ method is the 2-cyclopentylidenecyclopentanone (**1c**), which gives instead of the expected epoxide **3c** δ-valerolactone in 30% yield. Even at a controlled pH of 7.3–7.5 retroaldol reaction of **1c** to cyclopentanone takes place, and the latter suffers Baeyer-Villger rearrangement to δ-valerolactone. These complications can be prevented by using the isolated dimethyldioxirane (**2a**) as oxidant, which leads to the desired epoxide **3c** in 94% yield. Thus, for base- and acid-sensitive and hydrolytically labile substrates the isolated dimethyldioxirane procedure is mandatory.

The structure assignment of the epoxides **3a–r** rests on the carbonyl band at $\tilde{\nu}$ = 1660–1760 cm^{-1} in the IR spectrum. The epoxide proton signals occur at δ = 3.40–5.05

in the ^{1}H-NMR spectrum, and the ^{13}C-NMR resonance lines of the C-α and -β epoxide atoms at δ = 59–61. A moderate molecular ion peak appears in the mass spectra, and for the new derivatives **3q, r** satisfactory microanalyses have been obtained.

In summary, we have provided a superior epoxidation procedure of α,β-unsaturated ketones by using isolated dimethydioxirane (**2a**) and/or in situ generated ethyl(methyl)-dioxirane (**2b**). While the isolated dimethyldioxirane (**2a**) is particularly useful for the epoxidation of 2′-hydroxy-substituted chalcones and retroaldol-active substrates such as the cyclopentylidene derivative **1c**, the in situ generated ethyl-(methyl)dioxirane (**2b**) permits large-scale epoxidations. Our results show that dioxiranes are useful alternatives to the Weitz-Scheffer reaction (alkaline H_2O_2) for deactivated double bond.

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Experimental

Instrumentation and Materials: Melting points (not corrected): Reichert Thermovar hot-stage apparatus. – IR: Perkin-Elmer 1420. – ^{1}H and ^{13}C NMR: Bruker WM 200 (200 MHz) or WM 250 (250 MHz); chemical shifts refer to $CDCl_3$. – All solvents were purified by following standard literature methods; acetone, 2-butanone, and water used in the preparation of dioxirane (isolated or in situ) were doubly distilled from EDTA. Caroate (potassium monoperoxosulfate, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was used as received. **1a–c** were commercially available. The (*E*)-chalcones **1d–o** were obtained by the condensation[20] of the appropriate benzaldehydes and substituted acetophenones in AcOH under H_2SO_4 catalysis.

Preparation of **2a** *(as Acetone Solution):* A 4000-ml four-necked round-bottomed flask (Figure 1), which contained a mixture of water (254 ml), acetone (192 ml, 2.62 mol), and $NaHCO_3$ (144 g) was equipped with a mechanical stirrer, a gas inlet tube which extended to the bottom of the flask, and an air condenser (length 29 cm). The exit of the air condenser was connected to a right-angle tube (length 20 cm), compactly packed with cotton wool, to the top entry of a high-efficiency, double-jacketed spiral condenser; the latter was supplied with methanol as coolant (–78 to –85°C) from a Colora Ultra Kryomat (Model K120W). The bottom exit of the high-efficiency condenser was attached in succession to a 500-ml receiving flask and a cold trap, both cooled by means of a dry ice/ethanol bath. N_2 was passed through the reaction flask, while the solid Caroate (310 g, 0.51 mol) was added in five portions at 3-min intervals while stirring the mixture vigorously at room temperature (ca. 20°C). After the last addition, a moderate vacuum (60–100 Torr) was applied, and the effluent solution of **2a** (150 ml, 0.06–0.10 M) was collected in the cooled receiving flask (1–2% yield). The content of **2a** was determined by oxidation of phenyl methyl sulfide to its sulfoxide, the latter quantitated by ^{1}H NMR. The solution of **2a** in acetone was stored in the freezer (–20°C) over molecular sieves (4 Å) without significant decomposition over one week.

Epoxidation of α,β-Unsaturated Ketones **1a–r** *by* **2a** *(as Acetone Solution). – General Procedure:* The required amount of the solution of **2a** in acetone (0.062–0.085 M), which was dried over molecular sieves (4 Å) at –20°C, was added rapidly under N_2 to a solution of the α,β-unsaturated ketone **1a–r** (0.62–1.07 mmol) in absolute CH_2Cl_2 (10 ml). The stirring was continued for 12 h, and a new quantity of the solution of **2a** in acetone (0.062–0.085 M) was rapidly added. The stirring was continued for another 12 h, the solvent removed in vacuo (ca. 20°C/15 Torr), and the epoxides **3a–r** isolated in high purity and excellent yields (Table 1).

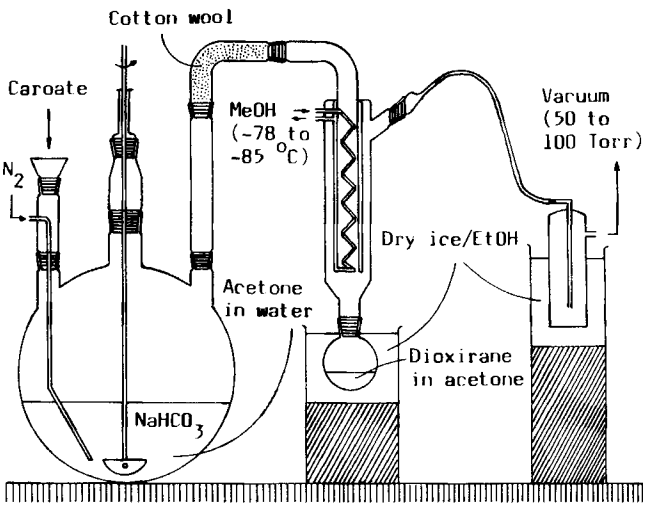

Figure 1. Simplified apparatus[9b] for the preparation of isolated dimethyldioxirane (**2a**)

$$Me_2CO \xrightarrow[\substack{pH \approx 7.4\\ ca.\ 20\,^\circ C}]{KHSO_5} \mathbf{2a}\,[\text{yellow solution (ca. 0.1 M) in } Me_2CO_2]$$

Table 1. Epoxidation of α,β-unsaturated ketones **1a–r** with dioxiranes **2a, b** to epoxides **3a–r**

1, 3	Method[a]	Yield (%)[b]	1, 3	Method[a]	Yield (%)[b]
a	A, B	86 (84) [90[21]]	**j**	A, B, C[e]	98 (100[f]) [ca. 100[26]]
b	A, B	90 (86) [78[22]]	**k**	A	99
c	A	94 (c) [47[23]]	**l**	A	99 [ca. 100[26]]
d	A, B	97 (93) [92[24]]	**m**	A	99 [94[28]]
e	A, B	ca. 100 (98) [75[15]]	**n**	A	96 [92[29]]
f	A, B	99 (93) [47[15]]	**o**	A	98 [66[30]]
g	A	ca. 100[d] [43[15]]	**p**	A	ca. 100 [20[18]]
h	A	ca. 100 [55[15]]	**q**	A	ca. 100
i	A, B	99 (94) [80[25]]	**r**	A	ca. 100

[a] A: Epoxidation with isolated **2a** in CH_2Cl_2/CH_3COCH_3 at ca. 20°C under N_2, ca. 20–24 h. B: Epoxidation with **2b** generated in situ from $KHSO_5/CH_3COCH_2CH_3$, phosphate buffer (pH ≈ 7.4) at ca. 20°C, ca. 48 h. C: Epoxidation with **2b** generated in situ from $KHSO_5/CH_3COCH_2CH_3$, CH_2Cl_2, $BuN^{\oplus}HSO_4^{\ominus}$, phosphate buffer (pH ≈ 7.4) at ca. 20°C, ca. 41 h. – [b] Yield of isolated pure product (values in parentheses refer to method B) [values in brackets refer to literature methods]. – [c] Instead of the expected epoxide **3c**, δ-valerolactone was obtained in 30% yield. – [d] 57% conversion. – [e] 89% yield. – [f] 40% conversion.

Epoxide **3a** (108 mg, 86%) was obtained as a colorless oil by following the above procedure at ca. 20°C for 20 h, in which a total of 21 ml of a 0.084 M (1.76 mmol) solution of **2a** and 113 mg (0.82 mmol) of **1a** were employed. – IR (CCl_4): $\tilde{\nu}$ = 2990 cm^{-1}, 2970, 2940, 1710, 1450, 1385, 1380, 1200, 1070, 1035, 980, 910. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.02 (s, 3H), 1.11 (s, 3H), 1.28–1.38 (m, 1H), 1.40 (s, 3H), 1.75–2.22 (m, 3H), 3.37–3.38 (m, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 16.2 (q), 20.7 (t), 24.8 (q), 25.3 (q), 30.0 (t), 41.7 (s), 57.1 (s), 61.0 (d), 209.7 (s).

Epoxide **3b** (121 mg, 90%) was obtained as a colorless oil by following the above procedure at ca. 20°C for 24 h, in which a total of 25 ml of a 0.085 M (2.10 mmol) solution of **2a** and 117 mg (0.85 mmol) of **1b** were employed. – IR (CCl_4): $\tilde{\nu}$ = 2980 cm^{-1}, 2940, 2920, 1725, 1465, 1400, 1370, 1350, 1310, 1280, 1255, 1200, 920. – ^1H NMR (250 MHz, $CDCl_3$): δ = 0.92 (s, 3H), 1.02 (s, 3H), 1.43 (s, 3H), 1.71 (dd, J_1 = 14.9 Hz, J_2 = 2.15 Hz, 1H), 1.78–1.84 (m, 1H), 2.08 (d, J = 14.9 Hz, 1H), 2.62 (d, J = 13.6 Hz, 1H), 5.05 (br. s, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 24.0 (q), 27.8 (q), 30.8 (q), 36.1 (s), 42.8 (t), 48.0 (t), 61.4 (d), 64.3 (s), 207.9 (s).

Epoxide **3c** (120 mg, 94%) was obtained as a colorless oil, by following the above procedure at ca. 20°C for 20 h, in which a total of 30 ml of a 0.062 M (1.86 mmol) solution of **2a** and 116 mg (0.77 mmol) of **1c** were employed. – IR (CCl_4): $\tilde{\nu}$ = 2980 cm^{-1}, 2880, 1760, 1450, 1410, 1230, 1210, 1165, 1020, 970. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.55–2.01 (m, 9H), 2.06–2.27 (m, 3H), 2.34–2.43 (m, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 17.9 (t), 24.9 (t), 25.4 (t), 27.3 (t), 29.5 (t), 31.9 (t), 37.2 (t), 67.9 (s), 76.7 (s), 173.2 (s).

Epoxide **3d** (135 mg, 97%) was obtained as colorless plates (from petroleum ether), m.p. 88–89°C (ref.[24] 90°C), by following the above procedure at ca. 20°C for 24 h, in which a total of 27 ml of a 0.062 M (1.57 mmol) solution of **2a** and 128 mg (0.62 mmol) of **1d** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3100 cm^{-1}, 3080, 3050, 1700, 1675, 1605, 1460, 1455, 1410, 1350, 1285, 1230, 1185, 1030, 1010, 910, 890, 705. – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.92 (d, J = 1.8 Hz, 1H), 4.16 (d, J = 1.8 Hz, 1H), 7.23 (s, 5H), 7.27–7.37 (m, 2H), 7.42–7.48 (m, 1H), 7.83–7.86 (m, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 59.4 (d), 61.0 (d), 125.9 (d), 128.7 (d), 128.8 (d), 128.9 (d), 129.0 (d), 134.1 (d), 135.5 (s), 135.6 (s), 193.1 (s).

Epoxide **3e** (192 mg, ca. 100%) was obtained as colorless needles (from petroleum ether), m.p. 75–77°C (ref.[15] 77–78°C), by following the above procedure at ca. 20°C for 24 h, in which a total of 30 ml of a 0.079 M (2.38 mmol) solution of **2a** and 180 mg (0.80 mmol) of **1e** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3070 cm^{-1}, 2970, 2950, 1700, 1680, 1450, 1400, 1290, 1235, 1010, 700. – ^1H NMR (250 MHz, $CDCl_3$): δ = 2.35 (s, 3H), 4.02 (d, J = 1.9 Hz, 1H), 4.29 (d, J = 1.9 Hz, 1H), 7.19 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.42–7.49 (m, 2H), 7.55–7.62 (m, 1H), 7.96–8.01 (m, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.2 (q), 59.4 (d), 61.0 (d), 125.8 (d), 128.3 (d), 128.8 (d), 129.4 (d) 132.4 (s), 133.9 (d), 135.4 (s), 139.0 (s), 193.1 (s).

Epoxide **3f** (202 mg, 99%) was obtained as colorless needles (from $CHCl_3$/petroleum ether), m.p. 82–83°C (ref.[15] 86–87°C), by following the above procedure at ca. 20°C for 24 h, in which a total of 35 ml of a 0.082 M (2.67 mmol) solution of **2a** and 190 mg (0.80 mmol) of **1f** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3080 cm^{-1} 3020, 2970, 2850, 1700, 1680, 1620, 1605, 1535, 1455, 1405, 1260, 1235, 1180, 1045, 700. – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.77 (s, 3H), 4.00 (d, J = 1.9 Hz, 1H), 4.31 (d, J = 1.9 Hz, 1H), 6.91 and 7.27 (AA'XX' system, 4H), 7.41–7.47 (m, 2H), 7.55–7.61 (m, 1H), 7.96–8.00 (m, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.3 (q), 59.4 (d), 60.9 (d), 114.2 (d), 127.2 (s), 127.3 (d), 128.3 (d), 128.8 (d), 133.9 (d), 134.4 (d), 160.3 (s), 193.2 (s).

Epoxide **3g** (153 mg, ca. 100%) was obtained after 57% conversion as colorless needles (from $CHCl_3$/petroleum ether), m.p. 148–150°C (ref.[15] 148–150°C), by following the above procedure at ca. 20°C for 24 h, in which a total of 30 ml of a 0.079 M (2.38 mmol) solution of **2a** and 202 mg (0.80 mmol) of **1q** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3080 cm^{-1}, 3060, 1695, 1675, 1600, 1530, 1450, 1350, 1230, 1215, 1110, 1010, 980, 845, 705. – ^1H NMR (250 MHz, $CDCl_3$): δ = 4.22 (d, J = 1.8 Hz, 1H), 4.31 (d, J = 1.8 Hz, 1H), 7.49–7.70 (m, 3H), 7.60 (dd, J_1 = 8.8 Hz, J_2 = 1.9 Hz, 2H), 8.00–8.04 (m, 2H), 8.27 (dd, J_1 = 8.8 Hz, J_2 = 1.9 Hz, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 58.0 (d), 60.8 (d), 124.1 (d), 126.7 (d), 128.4 (d), 129.0 (d), 134.4 (d), 135.2 (s), 142.8 (s), 148.3 (s), 192.1 (s).

Epoxide **3h** (254 mg, ca. 100%) was obtained as colorless needles (from petroleum ether), m.p. 83–84°C (ref.[15] 84–86°C), by following the above procedure at ca. 20°C for 24 h, in which a total of 45 ml of a 0.08 M (3.58 mmol) solution of **2a** and 237 mg (1.07 mmol) of **1h** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3080 cm^{-1}, 1715, 1690, 1625, 1480, 1300, 1245, 1195, 1015, 705. – ^1H NMR (250 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 4.03 (d, J = 1.9 Hz, 1H), 4.27 (d, J = 1.9 Hz, 1H). 7.23 (d, J = 8.1 Hz, 2H), 7.35 (s, 5H), 7.88 (dd, J_1 = 8.1 Hz, J_2 = 1.61 Hz, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.7 (q), 59.2 (d), 60.8 (d), 125.8 (d), 128.4 (d), 128.7 (d), 129.1 (d), 129.5 (d), 135.0 (s), 135.6 (s), 145.0 (s), 192.5 (s).

Epoxide **3i** (180 mg, 99%) was obtained as colorless plates (from ether/petroleum ether), m.p. 75–76°C (ref.[25] 97–80°C), by following the above procedure at ca. 20°C for 24 h, in which a total of 30 ml of a 0.071 M (2.14 mmol) solution of **2a** and 170 mg (0.71 mmol) of **1i** were employed. – IR (CCl_4): $\tilde{\nu}$ = 2980 cm^{-1}, 2850, 1690, 1670, 1610, 1520, 1430, 1265, 1245, 1180, 1040. – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 4.04 (d, J = 1.9 Hz, 1H), 4.25 (d, J = 1.9 Hz, 1H), 6.92 (d, J = 8.3 Hz, 2H), 7.35 (s, 5H), 7.98 (dd, J_1 = 8.9 Hz, J_2 = 1.9 Hz, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.5 (q), 59.1 (d), 60.7 (d), 114.1 (d), 125.8 (d), 128.5 (s), 128.7 (d), 128.9 (d), 130.7 (d), 135.7 (s), 164.2 (s), 191.3 (s).

Epoxide **3j** (238 mg, 98%) was obtained as colorless needles (from $CHCl_3$/petroleum ether), m.p. 127–128°C (ref.[25] 125°C), by following the above procedure at ca. 20°C for 24 h, in which a total of 27 ml of a 0.084 M (2.30 mmol) solution of **2a** and 230 mg (0.80 mmol) of **1j** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3080 cm^{-1}, 3050, 1695, 1670, 1610, 1590, 1410, 1280, 1230, 1180, 1075, 1010, 890, 700. – ^1H NMR (250 MHz, $CDCl_3$): δ = 4.07 (d, J = 1.9 Hz, 1H), 4.23 (d, J = 1.9 Hz, 1H), 7.34–7.44 (m, 5H), 7.60–7.65 (m, 2H), 7.85–7.91 (m, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 59.4 (d), 61.0 (d), 125.8 (d), 128.8 (d), 129.4 (s), 129.9 (d), 131.9 (d), 132.2 (d), 134.1 (s), 135.2 (s), 192.3 (s).

Epoxide **3k** (235 mg, 99%) was obtained as colorless powder (from EtOH), m.p. 101–102°C (ref.[27] 106°C) by following the above procedure at ca. 20°C for 24 h, in which a total of 30 ml a of 0.082 M (2.46 mmol) solution of **2a** and 223 mg (0.94 mmol) of **1k** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3030 cm^{-1}, 2920, 1690, 1670, 1610, 1425, 1410, 1290, 1245, 1230, 1180, 1010, 890. – ^1H NMR (250 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 2.38 (s, 3H), 3.99 (d, J = 1.9 Hz, 1H), 4.26 (d, J = 1.9 Hz, 1H), 7.17 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.1 Hz, 2H), 7.88 (dd, J_1 = 8.3 Hz, J_2 = 1.6 Hz, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.2 (q), 21.7 (q), 59.3 (d), 60.9 (d), 125.8 (d), 128.4 (d), 129.4 (d), 129.5 (d), 132.6 (s), 133.1 (s), 138.9 (s), 144.9 (s), 192.6 (s).

Epoxide **3l** (205 mg, 99%) was obtained as colorless plates (from ether/petroleum ether), m.p. 79–80°C (ref.[26] 79–80°C), by following the above procedure at ca. 20°C for 24 h, in which a total of 30 ml of a 0.071 M (2.14 mmol) solution of **2a** and 194 mg (0.77 mmol) of **1l** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3030 cm^{-1}, 2980, 2950, 1695, 1675, 1615, 1520, 1430, 1315, 1270, 1245, 1180, 1040. – ^1H NMR (250 MHz, $CDCl_3$): δ = 2.35 (s, 3H), 3.83 (s, 3H), 4.00 (d, J = 1.8 Hz, 1H), 4.24 (d, J = 1.8 Hz, 1H), 6.92 and 7.98 (AA'XX system, 4H), 7.18 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.2 (q), 55.5 (q), 59.2 (d), 60.8

(d), 114.1 (d), 125.8 (d), 128.6 (d), 129.4 (d), 130.7 (d), 132.7 (d), 138.9 (s), 164.2 (s), 191.4 (s).

Epoxide **3m** (231 mg, 99%) was obtained as colorless plates (from EtOH), m.p. 86–88°C (ref.[26] 109–110°C), by following the above procedure at ca. 20°C for 24 h, in which a total of 30 ml of a 0.082 M (2.46 mmol) solution of **2a** and 219 mg (0.87 mmol) of **1m** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3020 cm^{-1}, 2980, 2950, 1705, 1680, 1625, 1530, 1315, 1270, 1260, 1200, 1190, 1055. – ^1H NMR (250 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 3.76 (s, 3H), 3.98 (d, J = 1.8 Hz, 1H), 4.28 (d, J = 1.8 Hz, 1H), 6.88 and 7.26 (AA'XX' system, 4H, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.5 (q), 55.2 (q), 59.2 (d), 60.8 (d), 114.2 (d), 127.2 (d), 127.4 (s), 128.4 (d), 129.5 (d), 133.1 (s), 144.9 (s), 160.2 (s), 192.7 (s).

Epoxide **3n** (217 mg, 96%) was obtained as colorless powder (from EtOH), m.p. 114–116°C (ref.[29] 119–120°C) by following the above procedure at ca. 20°C for 24 h, in which a total of 35 ml of a 0.082 M (2.70 mmol) solution of **2a** and 214 mg (0.80 mmol) of **1n** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3060 cm^{-1}, 3010, 2980, 1715, 1695, 1635, 1550, 1280, 1265, 1200, 1060. – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.80 (s, 3H), 3.85 (s, 3H), 4.00 (d, J = 1.9 Hz, 1H), 4.26 (d, J = 1.9 Hz, 1H), 6.90 and 7.28 (AA'XX' system, 4H), 6.93 and 7.98 (AA'XX system, 4H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.3 (q), 55.5 (q), 59.2 (d), 60.8 (d), 114.1 (d), 114.7 (d), 127.2 (d), 127.5 (s), 128.6 (s), 130.7 (d), 160.2 (s), 164.2 (s), 191.5 (s).

Epoxide **3o** (264 mg, 98%) was obtained as colorless powder (from EtOH), m.p. 134–136°C (ref.[30] 136°C) by following the above procedure at ca. 20°C for 24 h, in which a total of 27 ml of a 0.084 M (2.40 mmol) solution of **2a** and 254 mg (0.80 mmol) of **2o** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3010 cm^{-1}, 2960, 1695, 1615, 1675, 1590, 1520, 1305, 1255, 1170, 1070, 1040, 1010. – ^1H NMR (200 MHz, $CDCl_3$): δ = 3.83 (s, 3H), 4.02 (d, J = 1.8 Hz, 1H), 4.23 (d, J = 1.8 Hz, 1H), 6.93 (d, J = 8.8 Hz, 2H), 7.28 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H), 7.88 (d, J = 8.7 Hz, 2H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.3 (q), 59.4 (d), 61.1 (d), 114.3 (d), 127.0 (s), 127.1 (d), 129.3 (s), 129.8 (d), 132.2 (d), 134.2 (s), 160.4 (s), 192.4 (s).

Epoxide **3p** (220 mg, ca. 100%) was obtained as colorless powder (from $CHCl_3$/petroleum ether), m.p. 73–74°C (ref.[18] 78°C) by following the above procedure at ca. 20°C for 24 h, in which a total of 35 ml of a 0.060 M (2.10 mmol) solution of **2a** and 205 mg (0.92 mmol) of **1p** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3070 cm^{-1}, 1660, 1630, 1500, 1460, 1370, 1295, 1255, 1220, 1165, 905. – ^1H NMR (250 MHz, $CDCl_3$): δ = 4.11 (d, J = 1.8 Hz, 1H), 4.33 (d, J = 1.8 Hz, 1H), 6.86–6.93 (m, 1H), 7.03 (dd, J_1 = 8.5 Hz, J_2 = 0.9 Hz, 1H), 7.35–7.46 (m, 5H), 7.48–7.55 (m, 1H), 7.81 (dd, J_1 = 8.1 Hz, J_2 = 1.6 Hz, 1H), 11.88 (s, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 59.7 (d), 59.8 (d), 118.7 (d), 118.8 (s), 119.4 (d), 125.8 (d), 128.8 (d), 129.2 (d), 129.4 (d), 135.1 (s), 137.3 (d), 162.6 (s), 197.3 (s).

Epoxide **3q** (221 mg, ca. 100%) was obtained as colorless powder (from petroleum ether), m.p. 59–60°C, by following the above procedure at ca. 20°C for 22 h, in which a total of 37 ml of a 0.070 M (2.60 mmol) solution of **2a** and 207 mg (0.87 mmol) of **1q** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3050 cm^{-1}, 1660, 1640, 1625, 1500, 1295, 1250, 1210, 1160, 720. – ^1H NMR (250 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 4.04 (d, J = 1.6 Hz, 1H), 4.30 (d, J = 1.6 Hz, 1H), 6.82–6.89 (m, 1H), 6.98 (d, J = 8.1 Hz, 1H), 7.21 (dd, J_1 = 14.5 Hz, J_2 = 8.2 Hz, 4H), 7.44–7.51 (m, 1H), 7.8 (dd, J_1 = 8.0 Hz, J_2 = 1.3 Hz, 1H), 11.89 (s, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 21.2 (q), 59.8 (d), 59.9 (d), 118.6 (d), 118.8 (s), 119.3 (d), 125.8 (d), 126.8 (d), 129.5 (d), 132.1 (s), 137.2 (d), 139.2 (s), 162.5 (s), 197.5 (s). – MS (70 eV): m/z (%) = 254 (25) [M^+], 225 (34) [M^+ – CHO], 133 (49) [M^+ – C_8H_9O], 121 (100) [M^+ – C_9H_9O], 105 (31) [M^+ – $C_9H_9O_2$], 77 (15) [M^+ – $C_{10}H_9O_3$].

$C_{16}H_{14}O_3$ (254.3) Calcd. C 75.58 H 5.55
Found C 75.46 H 5.27

Epoxide **3r** (218 mg, ca. 100%) was obtained as colorlesss powder (from $CHCl_3$/petroleum ether), m.p. 83–86°C, by following the above procedure at ca. 20°C for 21 h, in which a total of 47 ml of a 0.070 M (2.60 mmol) solution of **2a** and 206 mg (0.81 mmol) of **1r** were employed. – IR (CCl_4): $\tilde{\nu}$ = 3020 cm^{-1}, 2980, 1700, 1650, 1615, 1520, 1255, 1210, 1040. – ^1H NMR (250 MHz, $CDCl_3$): δ = 3.78 (s, 3H), 4.03 (d, J = 1.8 Hz, 1H), 4.32 (d, J = 1.8 Hz, 1H), 6.83–6.94 (m, 1H), 6.91 and 7.27 (AA'XX system, 4H), 6.99 (dd, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.45–7.52 (m, 1H), 7.79 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 11.98 (s, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 55.3 (q), 59.8 (d), 59.9 (d), 114.3 (d), 118.6 (d), 118.8 (d), 119.4 (d), 126.9 (s), 127.2 (d), 129.5 (d), 137.2 (d), 160.4 (s), 162.5 (s), 197.6 (s). – MS (70 eV): m/z (%) = 270 (18) [M^+], 241 (16) [M^+ – CHO], 150 (31) [M^+ – C_8H_8O], 133 (12) [M^+ – $C_8H_9O_2$], 121 (100) [M^+ – $C_9H_9O_2$], 77 (13) [M^+ – $C_{10}H_9O_4$].

$C_{16}H_{14}O_4$ (270.3) Calcd. C 71.10 H 5.22
Found C 70.57 H 5.06

Epoxidation of α,β-Unsaturated Ketones **1a, b, d–f, i, j** *by* **2b** *Generated in situ from Caroate and 2-Butanone. – General Procedure:* To a vigorously stirred (mechanical agitation) mixture of α,β-unsaturated ketone **1** (15.0 mmol), 2-butanone (25–150 ml), and phosphate buffer (prepared by dissolving 0.177 g of KH_2PO_4 and 0.648 g of Na_2HPO_4 in 150 ml of water) was added slowly (ca. 6.0 h) at room temperature (ca. 20°C), a saturated aqueous solution of Caroate [prepared by dissolving 30–45 g (0.05–0.075 mol) of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ in 150–200 ml of water]. The pH of the mixture was kept constant throughout the reaction at 7.3–7.5 with the help of 3% aqueous KOH. After 18 h of additional stirring, a new batch of saturated aqueous Caroate solution (cf. above) was slowly (ca. 6.0 h) added and stirred for an additional 18 h to bring the epoxidation to completion. Solid NaCl was added to the cloudy reaction mixture until saturation, the organic phase was separated by decantation, and the aqueous phase was extracted with CH_2Cl_2 (4 × 50 ml). The combined organic layers were dried with $MgSO_4$, the drying agent was removed by filtration, and the solvent evaporated (ca. 20°C/15 Torr) to afford the corresponding epoxide in high purity (NMR).

Epoxide **3a** (1.96 g, 84%) was obtained by following the above procedure, in which a total of 65.0 g (0.106 mol) of Caroate, 25 ml of 2-butanone, and 2.00 g (15.00 mmol) of **1a** were employed (for physical constants cf. above).

Epoxide **3b** (2.00 g, 86%) was obtained by following the above procedure, in which a total of 65.0 g (0.106 mol) of Caroate, 25 ml of 2-butanone, and 2.00 g (15.00 mmol) of **1b** were employed (for physical constants cf. above).

Epoxide **3d** (2.26 g, ca. 100% at 67% conversion) was obtained by following the above procedure, in which a total of 60.0 g (0.098 mol) of Caroate, 50 ml of 2-butanone, and 3.14 g (15.10 mmol) of **1d** were employed. Under optimized conditions, epoxide **3d** was obtained in 93% yield (after column chromatography) when 90 g (0.147 mol) of Caroate and 150 ml of 2-butanone were employed (for physical constants cf. above).

Epoxide **3e** (3.51 g, 98%) was obtained by following the above procedure, in which a total of 70.7 g (0.114 mol) of Caroate, 100 ml of 2-butanone, and 3.30 g (15.00 mmol) of **13** were employed (for physical constants cf. above).

Epoxide **3f** (3.20 g, 93% yield at 91% conversion) was obtained by following the above procedure, in which a total of 70.0 g (0.114 mol) of Caroate, 100 ml of 2-butanone, and 3.57 g (15.00 mmol) of **1f** were employed (for physical constants cf. above).

Epoxide **3i** (3.60 g, 94%) was obtained by following the above procedure, in which a total of 90.0 g (0.146 mol) of Caroate, 100 ml of 2-butanone, and 3.57 g (15.0 mmol) of **1i** were employed (for physical constants cf. above).

Epoxide **3j** (1.82 g, ca. 100% yield at 40% conversion) was obtained by following the above procedure, in which a total of 70.0 g (0.114 mol) of Caroate, 150 ml of 2-butanone, and 4.30 g (15.00 mmol) of **1j** were employed (for physical constants cf. above).

Epoxidation of **1j** *by* **2b** *Generated in situ from Caroate and 2-Butanone in* CH_2Cl_2 *and* $Bu_4N^{\oplus}HSO_4^{\ominus}$: To a vigorously stirred (mechanical agitation) mixture of 2.97 g (10.35 mmol) of **1j**, 100 ml of 2-butanone, 100 ml of CH_2Cl_2, phosphate buffer [prepared by dissolving 0.177 g of KH_2PO_4 and 0.648 g of Na_2HPO_4 in 150 ml of water] and 0.5 g of $Bu_4N^{\oplus}HSO_4^{\ominus}$, was added slowly (ca. 7.0 h) a saturated aqueous solution of Caroate [prepared by dissolving 45 g (0.075 mol) of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ in 200 ml of water]. The pH of the mixture was kept constant throughout the reaction at 7.3–7.5 with the help of 3% aqueous KOH. After 16 h of additional stirring, a new batch of saturated aqueous Caroate solution (cf. above) was slowly (ca. 6.0 h) added and stirred for an additional 13 h. Solid NaCl was added to the cloudy reaction mixture until saturation, the organic phase was separated by decantation, and the aqueous phase was extracted with CH_2Cl_2 (4 × 50 ml). The combined organic layers were dried with $MgSO_4$, the drying agent was removed by filtration, the solvent evaporated (ca. 20°C/15 Torr), and the residue chromatographed (silica gel; CH_2Cl_2 as eluant) to afford epoxide **3j** (2.80 g, 89%) as colorless needles (from EtOH), m.p. 127–129°C (ref.[8] 125°C) (for spectral data cf. above).

Reaction of **1c** *with* **2b** *Generated in situ from Caroate and 2-Butanone:* δ-Valerolactone (0.450 g, 30%; ref.[31] 88%) was obtained as colorless oil by following the above procedure in which a total of 60.0 g (0.098 mol) of Caroate, 25 ml of 2-butanone, and 2.25 g (15.00 mmol) of **1c** were employed. – IR (CCl_4): $\tilde{\nu}$ = 2950 cm^{-1}, 2890, 1740, 1390, 1340, 1270, 1250, 1230, 1150, 1080, 1050, 1010, 930. – ^1H NMR (250 MHz, $CDCl_3$): δ = 1.82–1.98 (m, 4H), 2.55 (t, *J* = 6.9 Hz, 2H), 4.32–4.36 (m, 2H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.1 (t), 22.3 (t), 29.9 (t), 69.5 (t), 171.5 (s).

CAS Registry Numbers

1a: 20013-73-4 / **1b**: 78-59-1 / **1c**: 825-25-2 / **1d**: 614-47-1 / **1e**: 22252-14-8 / **1f**: 22252-15-9 / **1g**: 2960-55-6 / **1h**: 14802-30-3 / **1i**: 22966-19-4 / **1j**: 22966-23-0 / **1k**: 13565-37-2 / **1l**: 41564-65-2 / **1m**: 50990-40-4 / **1n**: 41564-67-4 / **1o**: 126443-12-7 / **1p**: 888-12-0 / **1q**: 34000-27-6 / **1r**: 34000-29-8 / **2a**: 74087-85-7 / **2b**: 58272-12-1 / **3a**: 29974-13-8 / **3b**: 10276-21-8 / **3c**: 36803-49-3 / **3d**: 7570-86-7 / **3e**: 27729-96-0 / **3f**: 27729-95-9 / **3g**: 27730-03-6 / **3h**: 32157-66-7 / **3i**: 18873-03-5 / **3j**: 32157-71-4 / **3k**: 32383-89-4 / **3l**: 32383-88-3 / **3m**: 32383-87-2 / **3n**: 105782-42-1 / **3o**: 130248-88-3 / **3p**: 129878-47-3 / **3q**: 130248-89-4 / **3r**: 129878-46-2

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