# Novel Cyclic Ketones for Catalytic Oxidation Reactions

Dan Yang,* Yiu-Chung Yip, Man-Wai Tang, Man-Kin Wong, and Kung-Kai Cheung

*Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong*

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In our effort to search for $C_2$ symmetric and conformationally rigid chiral ketones as catalysts for asymmetric epoxidation, a series of cyclic ketones **4**−**10** were prepared from the corresponding diacids. Compared with acyclic ketones for epoxidation of *trans*-stilbene, those 9-, 10-, and 11-membered-ring cyclic ketones were found to have much higher catalytic activities, which were attributed to steric effects, electronic effects, and ring strains. By using the homogeneous acetonitrile−water solvent system, unfunctionalized olefins with various substitution patterns (with 5 mol % of ketone **9**) and strongly electron-deficient olefins (with a 1:1 ketone **9**:substrate ratio) were epoxidized with Oxone as terminal oxidant in 75−96% yield at room temperature and neutral pH. In addition, oxidation of alcohols (with 20 mol % of ketone **9**) was carried out successfully with good isolated yields of aldehydes or ketones (75−88%).

## I. Introduction

Dioxiranes[1] are important oxidants for organic reactions such as epoxidation,[2] heteroatom oxidation,[3] and oxygenation of C−H bonds.[4] In particular, epoxidation mediated by dioxiranes is stereospecific and highly efficient toward both electron-rich[5] and electron-deficient olefins.[6] In the past several years, substantial progress has been made in developing chiral ketone catalysts[7−12] for asymmetric epoxidation of a variety of olefins with excellent enantioselectivity. As the first step in our program to develop $C_2$ symmetric chiral ketones for catalytic asymmetric epoxidation,[8a−c] it is essential to search for highly efficient ketone catalysts in which the desired chiral element can be incorporated. In addition, the design and synthesis of a cheap, robust, recyclable, and environmentally friendly catalyst for epoxidation with low catalyst loading[10,13−15] is still a great challenge. Using our *in situ* epoxidation protocol in which dioxiranes are generated effectively from ketones and Oxone in a homogeneous acetonitrile−water solvent system,[16] we have carried out a search for efficient ketone catalysts.

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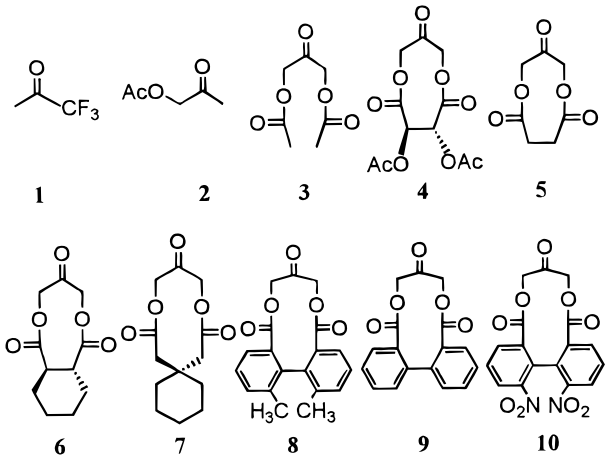
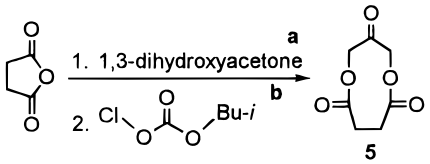
**Chart 1**




**Scheme 1. The Synthetic Pathway of Ketone 5**[a]




[a] (a) THF, reflux, 20 h; (b) $Et_3N$, THF, −5 °C to rt; reflux, 15 h.

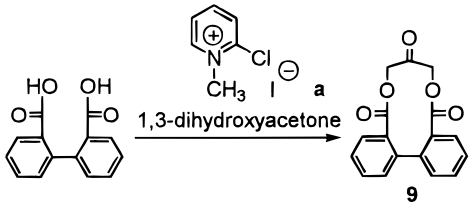
Here we report that a series of cyclic ketones of 2-fold symmetry have unprecedented activities in oxidation reactions. A portion of this work was published earlier.[8a,c]

## II. Results and Discussion

**Rational Design of Ketones 4−10 for Catalytic Epoxidation of *trans*-Stilbene.** We previously reported that (1) ketones with electron-withdrawing groups, such as F, Cl, and OAc, at α-positions would show higher activities in catalyzing epoxidation reactions; and (2) steric hindrance at α-positions would decrease the activity of a ketone.[8a] Therefore, a series of 2-fold symmetric and conformationally rigid cyclic analogues of 1,3-diacetoxyacetone **3** (ketones **4**−**10**; Chart 1) were examined for their catalytic activities in oxidation reactions. This series of ketones were found to be efficient catalysts for not only epoxidation of various olefins but also oxidation of alcohols.

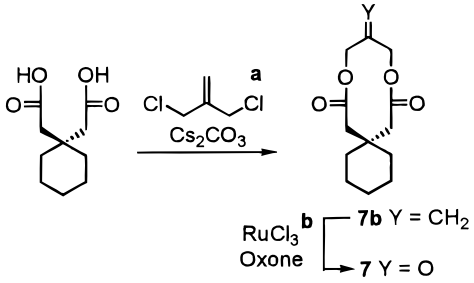
**Preparation of Cyclic Ketones 4−10.** Ketones **4** and **5** were prepared in 6−22% overall yield by refluxing the corresponding acid anhydrides with 1,3-dihydroxyacetone and subsequent intramolecular cyclization with isobutylchloroformate and triethylamine.[17] The synthetic scheme of ketone **5** is illustrated as an example (Scheme 1). Ketones **6** and **8**−**10** were prepared in one step (20−45% yield) from the corresponding diacids and 1,3-dihydroxyacetone using 2-chloro-1-methylpyridinium iodide (Mukaiyama reagent).[18] The synthetic scheme of ketone **9** is illustrated as an example (Scheme 2). As shown in Scheme 3, ketone **7** was prepared by the coupling of the corresponding diacid with 3-chloro-2-chloromethyl-1-propene in the presence of $Cs_2CO_3$[19] (67% yield) and subsequent cleavage using $RuCl_3$/Oxone[20] (90% yield). The synthetic pathway also applies to the preparation of ketone **9**.

**Scheme 2. The Synthetic Pathway of Ketone 9**[a]




[a] (a) $Et_3N$, $CH_3CN$, rt, 12 h.

**Scheme 3. The Synthetic Pathway of Ketone 7**[a]




[a] (a) DMF, 95 °C, 10 h, (b) $NaHCO_3$, $CH_3CN$, $H_2O$, rt, 40 min.

**Catalytic Activities of Ketones 1−10 in the Epoxidation of *trans*-Stilbene.** The results of the epoxidation of *trans*-stilbene catalyzed by ketones **1**−**10** (Chart 1) are summarized in Table 1. Several interesting features were observed. (1) With a 1:1 ketone:substrate ratio at rt, epoxidation of *trans*-stilbene catalyzed by cyclic ketones **5**−**10** proceeded faster than those catalyzed by 1,1,1-trifluoroacetone **1** and acyclic ketones **2**−**3**. (2) The activities of cyclic ketones were found to increase in the order of 9-membered-ring ketones **4**−**6** < 10-membered-ring ketone **7** < 11-membered-ring ketones **8**−**10** and were dramatically affected by their remote substituents as well (for example, entries 4−6). Among those ketones screened, ketone **10** showed the highest catalytic activity. (3) No considerable ketone-catalyzed Oxone decomposition was observed for all ketones screened. Only 3−4 equiv of Oxone was required for those epoxidation reactions. (4) Cyclic ketones **6**−**10** were stable under the reaction conditions but not very stable toward silica gel. Therefore, triethylamine was added to buffer the silica gel during flash column purification. Ketones **6**−**10** were recovered in high yield (over 80%) and reused without loss of catalytic activities. (5) To demonstrate the catalytic efficiency of cyclic ketones, epoxidation of *trans*-stilbene was carried out using 1 mol % of ketone **9** at rt. The reaction was complete in 12 h, and *trans*-stilbene epoxide was isolated in 98% yield.

**Studies of Hydration Equilibrium Constants.** Two steps are involved in the generation of dioxiranes *in situ* (Figure 1): nucleophilic addition of Oxone ($HSO_5^-$) to ketones and the cyclic peroxide formation.[13a,21] For maximium dioxirane formation, the addition of Oxone to the ketone carbonyl group should be favorable. Because the common feature for addition of both Oxone and water to the ketone is rehybridization of the carbonyl carbon from

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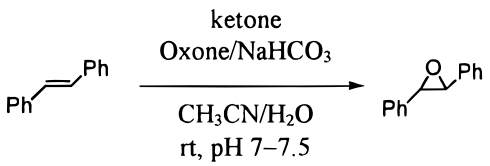
**Table 1. Activities of Ketones 1−10 in Catalyzing *in Situ* Epoxidation of *trans*-Stilbene with a 1:1 Ketone:Substrate Ratio[a] and Hydration Equilibrium Constants for Ketones 3 and 6−10[b]**




| entry | ketone | $K$ ($M^{-1}$) | reactn time (min)[c] | epoxide yield (%)[d] | ketone recovery (%) |
|---|---|---|---|---|---|
| 1 | **1** | *e* | 30 | 96 | *f* |
| 2 | **2** | *e* | 120 | 91 | 81[g] |
| 3 | **3** | 0.90 | 50 | 90 | 85[g] |
| 4 | **4** | *e* | 35 | 98 | 29[h] |
| 5 | **5** | *e* | 20 | 96 | 30[h] |
| 6 | **6** | 0.68 | 12 | 97 | 80[g] |
| 7 | **7** | 7.85 | 10 | 96 | 82[g] |
| 8 | **8** | 1.60 | 10 | 91 | 81[g] |
| 9 | **9** | 0.70 | 7 | 99 | 93[g] |
| 10 | **10** | 3.98 | 6 | 93 | 88[g] |

[a] Unless otherwise stated, reaction conditions were as follows: rt, 0.1 mmol of ketone, 0.1 mmol of *trans*-stilbene, 0.4 mmol of Oxone, 1.24 mmol of $NaHCO_3$, 1.5 mL of $CH_3CN$, 1.0 mL of aqueous $Na_2$·EDTA solution ($4 \times 10^{-4}$ M). [b] $K = K_{eq}[H_2O] = 55.5K_{eq}$ (at 20 °C); $K_{eq}$ = [hydrate]/{[ketone][$H_2O$]/2.5}. For determination of hydration equilibrium constants for ketones **3** and **6−10**, see Supporting Information. [c] Time for epoxidation to complete as shown by TLC. [d] Isolated yield after flash column chromatography. [e] Not determined. [f] Not attempted as the low boiling point (22 °C) of ketone **1** assures complete removal during the workup. [g] Flash column purification with $Et_3N$. [h] Flash column purification without $Et_3N$.

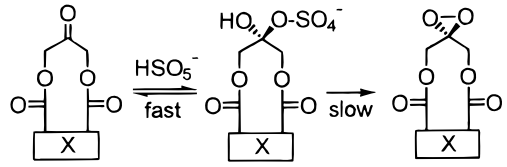



**Figure 1.**

sp$^2$ to sp$^3$, the hydration equilibrium constants may be used as an indicator of the stability of the tetrahedral adduct of the ketone and Oxone. As shown in Table 1, ketones **3** and **6−10** all showed moderate hydration ($K$ > 0.6 $M^{-1}$). However, we found that there was no direct correlation between the activities of ketones in catalyzing epoxidation and their hydration equilibrium constants.

**Structural Analysis of Cyclic Ketones.** The fact that medium-sized-ring cyclic ketones **4−10** have excellent catalytic efficiencies compared with that of acyclic ketone **3** may be understood by considering their structural properties. Given that ketones **3−10** are similarly activated by the electron-withdrawing inductive effects of the ester groups, cyclic ketones **4−10** with the two ester groups at α-positions folded back in the ring are sterically less hindered than ketone **3** and, thus, more reactive. Moreover, the dipoles of the ester groups in cyclic ketones **4−10** are opposite in direction to that of the keto group (Figure 2), which provides further activation for those cyclic ketones by the field effect. Therefore, cyclic ketones **4−10** should be more electrophilic than acyclic ketone **3**, which renders easier formation of cyclic dioxiranes from ketones **4−10**. On the other hand, following the above steric and electronic arguments for ketones, cyclic dioxiranes generated from ketones **4−10** are also expected to be more reactive than the linear one generated from ketone **3**.

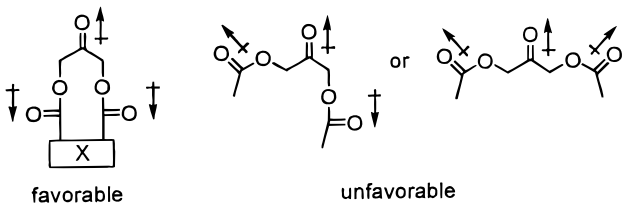



**Figure 2.**

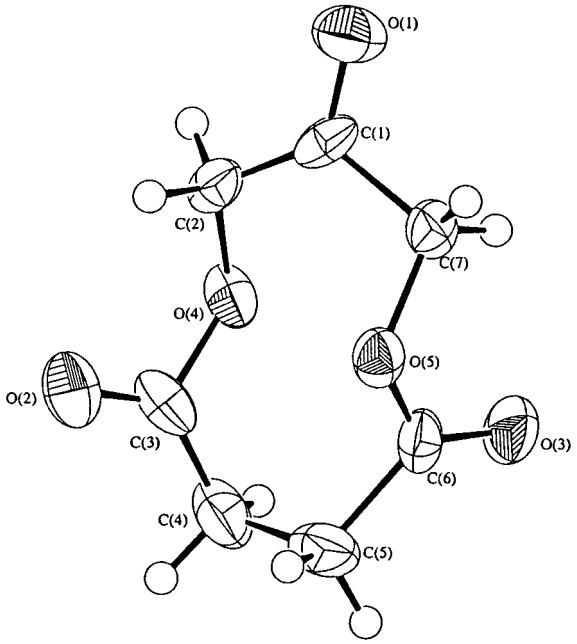



**Figure 3.** X-ray structure of ketone **5** (ORTEP view).

As revealed by the X-ray structures of ketones **5** (Figure 3) and **9** (Figure 4),[22] both the 9- and 11-membered-ring ketones have 2-fold symmetry with the keto groups lying on the 2-fold axes and the two ester groups of *s-trans* geometry. Selected bond angles and dihedral angles of ketones **5** and **9** are shown in Table 2. While the respective bond angles of ∠C−CO−C, ∠CO−C−O, ∠C−O−CO, and ∠O−CO−C are found to be similar for ketones **5** and **9**, the dihedral angle of the ester group (∠C−O−CO−C) increased remarkably from 158° in 9-membered-ring ketone **5** to about 176° in 11-membered-ring ketone **9**. Interestingly, the extent of ester bending (deviation from its ideal 180° plane), indicating ring strains of those cyclic ketones, seemed to correlate with the activities of these two cyclic ketones in catalyzing *in situ* epoxidation. Theoretical calculations revealed that the bond angle ∠C−C($O_2$)−C of dimethyldioxirane is about 117.7°,[23] very close to the bond angle ∠C−CO−C of acetone (117.2°). Therefore, dioxiranes

(22) Crystal data of ketone **5**: $C_7H_8O_5$, monoclinic, *Cc* (No. 9) with $a$ = 6.388(3) Å, $b$ = 15.594(2) Å, $c$ = 7.874(4) Å, $\beta$ = 109.15(4)°, $V$ = 740.9(6) Å$^3$, $Z$ = 4, $D_c$ = 1.543 g cm$^{-1}$, with 451 reflections refined on 672 reflections having $I > 3.0\sigma(I)$, $R$ = 0.046, and $R_w$ = 0.056. Crystal data of ketone **9**: $C_{17}H_{12}O_5$, monoclinic, $P2_1/n$ (No. 14) with $a$ = 14.503(3) Å, $b$ = 6.766(2) Å, $c$ = 15.709(5) Å, $\beta$ = 117.04(1)°, $V$ = 1373.0(5) Å$^3$, $Z$ = 4, $D_c$ = 1.433 g cm$^{-1}$, with 2430 reflections refined on 2470 reflections having $I > 3.0\sigma(I)$, $R$ = 0.044, and $R_w$ = 0.049. (The details of the X-ray analysis are provided as Supporting Information.)

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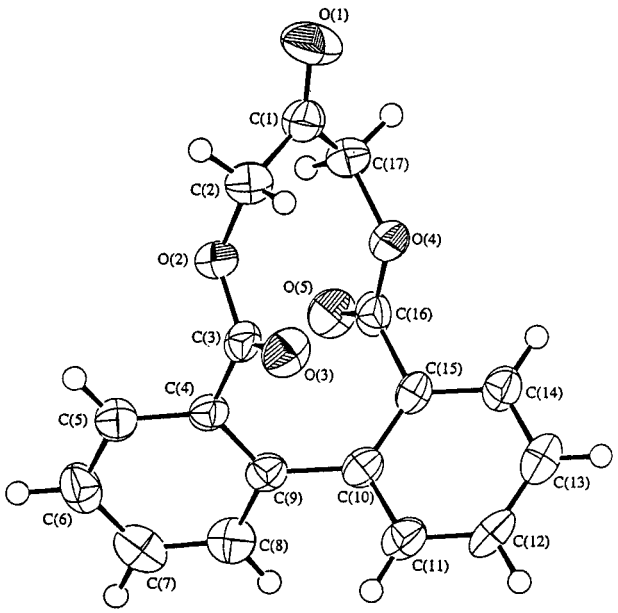



**Figure 4.** X-ray structure of ketone **9** (ORTEP view).

**Table 2. Selected Bond Angles and Dihedral Angles of Ketones 5 and 9**

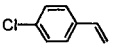
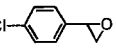
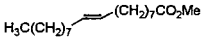
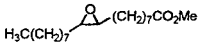
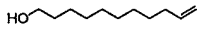
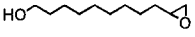
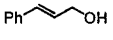
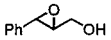
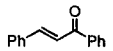
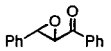
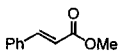
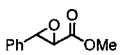
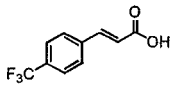
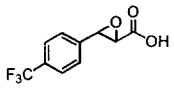
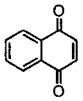
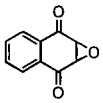
| | ketone **5** | ketone **9** |
|---|---|---|
| bond angle (deg) | | |
| ∠C−CO−C | 122.8 | 119.8 |
| ∠CO−C−O | 108.1 | 111.6 |
| ∠C−O−CO | 118.3 | 116.9 |
| ∠O−CO−C | 111.1 | 109.8 |
| dihedral angle (deg) | | |
| ∠CO−C−O−CO | 111.1 | 119.3 |
| ∠C−O−CO−C | 158.1 | 175.9 |

generated from less strained ketones are expected to be more stable and more readily formed. This possibly accounts for the higher activity of ketone **9** than that of ketone **5**. The strong field effect of the nitro groups can further enhance the electrophilicity of ketone **10**, which shows the highest activity among ketones **4**−**10**.

***In Situ* Epoxidation of Olefins Catalyzed by Ketone 9.** As one of the most efficient catalysts, ketone **9** was chosen for further screening with a variety of substrates. The results are summarized in Table 3. With 5 mol % of ketone **9** as the catalyst, epoxidation of simple olefins (entries 1−9) with 2 equiv of Oxone at rt can be finished at appreciable rates with excellent isolated yields of epoxides (75−96%). As the pH of the reaction mixture is maintained at 7−7.5 by sodium bicarbonate, those acid- or base-labile epoxides (entries 4, 6, and 8) can be easily isolated without decomposition. In addition, epoxidation of electron-deficient olefins (such as α,β-unsaturated ketones, esters, and acids; entries 10−14) with a 1:1 ketone **9**:substrate ratio at rt can be finished in 1−6 h, which is comparable in rate to those reactions catalyzed by trifluoroacetone **1** with a 10:1 ketone:substrate ratio at 0 °C. Besides, in all epoxidation reactions, ketone **9** can be recovered by flash column chromatography in over 90% yield.

**Catalytic Oxidation of Alcohols.**[24] Apart from epoxidation reactions, oxidation of various alcohols with 2 equiv of Oxone in the presence of 20 mol % of ketone **9** at rt can be finished in a reasonable period of time (3.2−12 h). The results are summarized in Table 4. 4-*tert*-Butylbenzyl alcohol was oxidized to 4-*tert*-butylbenzaldehyde in 77% isolated yield (entry 1). Secondary benzylic alcohols[25] were efficiently oxidized to the corre-

**Table 3. *In Situ* Epoxidation[a] Catalyzed by Ketone 9[b]**

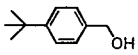
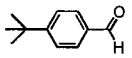
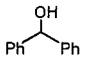
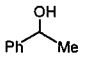
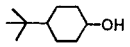
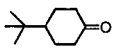
| entry | substrate | time (min)[c] | product | yield (%)[d] |
|---|---|---|---|---|
| 1 |  | 80 |  | 94 (Ref. 8c) |
| 2 |  | 160 |  | 91 (Ref. 8c) |
| 3 |  | 120 |  | 86 (Ref. 8c) |
| 4 |  | 60 |  | 75 (Ref. 8c) |
| 5 |  | 80 |  | 81 (Ref. 8c) |
| 6 |  | 60 |  | 80 (Ref. 8c) |
| 7 |  | 330 |  | 96 (Ref. 29) |
| 8 |  | 300 |  | 94 (Ref. 30) |
| 9 |  | 150 |  | 92 (Ref. 31) |
| 10[e] |  | 60 (80[f]) |  | 96 (Ref. 6b) |
| 11[e] |  | 90 (90[f]) |  | 89 (Ref. 32) |
| 12[e] |  | 120 (120[f]) |  | 96 (Ref. 33) |
| 13[e] |  | 120 (120[f]) |  | 85 (Ref. 16) |
| 14[e] |  | 360 (540[f,g]) |  | 88 (Ref. 34) |

[a] Unless otherwise stated, reaction conditions were as follows: rt, 0.01 mmol (5 mol %) of ketone **9**, 0.2 mmol of substrate, 0.4 mmol of Oxone, 1.24 mmol of $NaHCO_3$, 1.5 mL of $CH_3CN$, 1.0 mL of aqueous $Na_2$·EDTA solution ($4 \times 10^{-4}$ M). [b] Ketone **8** was recovered in over 90% yield by flash column chromatography with $Et_3N$ buffered silica gel. [c] Time for epoxidation to complete as shown by TLC. [d] Isolated yield after flash column chromatography. [e] 0.1 mmol of ketone **9**, 0.1 mmol of substrate, 0.5 mmol of Oxone, 1.55 mmol of $NaHCO_3$. [f] The value in parentheses was the reaction time for epoxidation carried out under the following conditions: 0 °C, 0.1 mmol of substrate, 1.0 mmol of trifluoroacetone, 0.5 mmol of Oxone, 1.55 mmol of $NaHCO_3$, 1.5 mL of $CH_3CN$, 1.0 mL of aqueous $Na_2$·EDTA solution ($4 \times 10^{-4}$ M). [g] 82% conversion as determined by $^1H$ NMR.

(24) For recent examples of catalytic oxidation of alcohols, see: (a) Ley, S. V.; Norman, J.; Griffith, W. P.; Marsden, S. P. *Synthesis* **1994**, 639. (b) Marko, I. E.; Giles, P. R.; Tsukazaki, M.; Brown, S. M.; Urch, C. J. *Science* **1996**, *274*, 2044. (c) Marko, I. E.; Giles, P. R.; Tsukazaki, M.; Chelle-Regnaut, I.; Urch, C. J., Brown, S. M. *J. Am. Chem. Soc.* **1997**, *119*, 12661. (d) De Mico, A.; Margarita, R.; Parlanti, L.; Vescovi, A.; Piancatelli, G. *J. Org. Chem.* **1997**, *62*, 6974. (e) Fung, W.-H.; Yu, W.-Y.; Che, C.-M. *J. Org. Chem.* **1998**, *63*, 2873.

(25) For oxidation of α-methylbenzyl alcohols by excess amounts of dimethyldioxirane, see: Kovac, F.; Baumstark, A. L. *Tetrahedron Lett.* **1994**, *35*, 8751.

**Table 4. *In Situ* Oxidation of Alcohols[a] Catalyzed by Ketone 9[b]**

| entry | substrate | time (h) | product | yield (%)[c] |
|---|---|---|---|---|
| 1 |  | 12[d] |  | 77 |
| 2 |  | 3.2[d] |  | 88 |
| 3 |  | 3.5[d] |  | 80 |
| 4 |  | 5[e] |  | 94 |
| 5 |  | 4[d] |  | 75 |
| 6 |  | 3.5[e] |  | 91 |
| 7 |  | 4[e] |  | 95 |

[a] Unless otherwise stated, reaction conditions were as follows: rt, 0.06 mmol (20 mol %) of ketone **9**, 0.3 mmol of substrate, 0.6 mmol of Oxone, 1.86 mmol of $NaHCO_3$, 1.5 mL of $CH_3CN$, 1.0 mL of aqueous $Na_2$·EDTA solution ($4 \times 10^{-4}$ M). [b] Ketone **9** was recovered in over 90% yield by flash column chromatography with $Et_3N$ buffered silica gel. [c] Isolated yield after flash column chromatography. [d] Time for oxidation to complete as shown by TLC. [e] The conversion was quantitative as determined by GLC.

sponding ketones in 80−94% yield (entries 2−4). Cyclic secondary alcohols were oxidized to ketones in 75−95% yield without the formation of the Baeyer−Villiger products (entries 5−7). Again, the ketone catalyst can be recovered in over 90% yield by column chromatography. To the best of our knowledge, this is the first report of ketone-catalyzed oxidation of alcohols with Oxone.

However, we should point out that oxidation of unactivated primary alcohols such as 2-phenylethanol with ketone **9** as catalyst was found to be ineffective. For substrates such as 10-undecen-1-ol (Table 3, entry 8) and cinnamyl alcohol (Table 3, entry 9), the olefinic double bonds were oxidized instead of the primary hydroxyl groups.

## III. Conclusion

In this paper, we have demonstrated that the readily available cyclic ketones **5**−**10** have exceptional activities in catalyzing the oxidation of olefins. The steric and electronic effects as well as ring strains contribute significantly to the catalytic activities of those cyclic ketones. Epoxidation of various olefins and oxidation of alcohols catalyzed by ketone **9** can be finished at appreciable rates with excellent isolated yields of products and ketone recovery (>90%). These oxidation reactions are green processes as the terminal oxidant Oxone only produces nontoxic potassium hydrogen sulfate and oxygen as the byproducts. We believe a robust, recyclable, and environmentally friendly catalyst like ketone **9** should have great potential to be used as a benchtop catalyst for many other oxidation reactions.

## IV. Experimental Section

The olefins, alcohols, and Oxone were purchased from Aldrich Chemical Co. and used without further purification. The known epoxides were identified by comparison of the spectral and physical data with those reported.

**Preparation of Ketone 4.** (+)-Di-*O*-acetyltartaric anhydride[26] (0.67 g, 3.08 mmol) and 1,3-dihydroxyacetone (0.28 g, 3.08 mmol) were dissolved in THF (8 mL). The resulting solution was refluxed under $N_2$ atmosphere for 20 h. After dilution with $CH_2Cl_2$, the organic phase was washed with saturated $NaHCO_3$ solution and brine. The combined organic layers were dried over anhydrous $Na_2SO_4$, filtered, and concentrated to a white solid (0.58 g), which was used in the next step without further purification. The crude solid (0.52 g, 1.69 mmol) was dissolved in THF (10 mL) and treated with $Et_3N$ (0.28 mL, 2.04 mmol). The reaction mixture was stirred at −5 °C for 10 min. Isobutyl chloroformate (0.24 mL, 1.87 mmol) was added dropwise to the reaction mixture. The mixture was stirred at −5 °C for 10 min and at rt for 20 min. After dilution with THF (160 mL), the mixture was refluxed for 15 h. The solvent was evaporated off under reduced pressure. The residue was diluted with $CH_2Cl_2$ and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous $Na_2SO_4$, filtered, and concentrated. The residue was purified by flash column chromatography (10% to 35% EtOAc in hexane) to give ketone **4** (86 mg, 22% yield) as a white solid: analytical TLC (silica gel 60), 50% EtOAc in hexane, $R_f = 0.48$; mp 152−154 °C; $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 5.67 (d, $J = 16.9$ Hz, 2H), 5.24 (s, 2H), 4.38 (d, $J = 16.4$ Hz, 2H), 2.23 (s, 6H); $^{13}$C NMR (67.94 MHz, $CDCl_3$) $\delta$ 199.56, 169.74, 165.91, 71.86, 69.11, 20.35; IR ($CCl_4$) 1788, 1765, 1735 cm$^{-1}$; HRMS for $C_{11}H_{12}O_9$ ($M^+$) calcd 288.0481, found 288.0476; CIMS *m*/*z* 288 ($M^+$, 14), 198 (100).

**Preparation of Ketone 5.** Succinic anhydride (2.5 g, 25 mmol) and 1,3-dihydroxyacetone (2.25 g, 25 mmol) were dissolved in THF (80 mL). The resulting solution was refluxed under $N_2$ atmosphere for 20 h. Solvent removal by evaporation provided a white solid (4.7 g), which was used in the next step without further purification. The crude soild (2 g, 10.5 mmol) was dissolved in THF (50 mL) and treated with $Et_3N$ (1.8 mL, 12.6 mmol). The reaction mixture was stirred at −5 °C for 10 min. Isobutyl chloroformate (1.5 mL, 11.6 mmol) was added dropwise to the reaction mixture. The mixture was stirred at −5 °C for 10 min and at rt for 20 min. After dilution with THF (150 mL), the mixture was refluxed for 15 h. The solvent was evaporated off under reduced pressure. The residue was diluted with $CH_2Cl_2$ and washed with saturated $NaHCO_3$ solution and brine. The organic layer was dried over anhydrous $Na_2SO_4$, filtered, and concentrated. The residue was purified by flash column chromatography (40% EtOAc in hexane) to give ketone **5** (109 mg, 6% yield) as a white solid: analytical TLC (silica gel 60), 50% EtOAc in hexane, $R_f = 0.5$; $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 4.94 (s, 4H), 2.72 (s, 4H); $^{13}$C NMR (67.94 MHz, $CDCl_3$) $\delta$ 202.14, 171.17, 68.93, 32.54; IR ($CCl_4$) 1769, 1738 cm$^{-1}$; HRMS for $C_7H_8O_5$ ($M^+$) calcd 172.0372, found 172.0367; EIMS (20 eV) *m*/*z* 173 ($M^+ + 1$, 55), 159 (100).

**Preparation of Ketone 6.** *trans*-1,2-Cyclohexanedicarboxylic acid (344 mg, 2 mmol) and 1,3-dihydroxyacetone (270 mg, 3 mmol) were dissolved in anhydrous $CH_3CN$ (200 mL). Triethylamine (1.8 mL, 12 mmol) was added to the reaction mixture. The resulting solution was stirred at rt for 15 min, followed by addition of 2-chloro-1-methylpyridinium iodide (1.22 g, 4.8 mmol). The reaction mixture was refluxed under $N_2$ atmosphere for 15 h. The solvent was evaporated off under reduced pressure. The dark-brown residue was diluted with $CH_2Cl_2$. The organic phase was washed twice with $H_2O$, dried over anhydrous $Na_2SO_4$, filtered, and concentrated. The residue was purified by flash column chromatography: 40 g of silica gel (Merck, 230−400 mesh) in hexane (300 mL) and $Et_3N$ (3 mL) was poured into a column of 30 mm diameter. The column was eluted with hexane followed by 30% EtOAc in hexane to give ketone **6** (122 mg, 24% yield) as a white solid: analytical TLC (silica gel 60), 30% EtOAc in hexane, $R_f = 0.52$; mp 84−85 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.68 (d, $J = 16.6$ Hz, 2H), 4.19 (d, $J = 16.6$ Hz, 2H), 2.49−2.45 (m, 2H), 2.00−1.71 (m, 6H), 1.36−1.26 (m, 2H); $^{13}$C NMR (125.76 MHz, $CDCl_3$) $\delta$ 202.66, 173.40, 68.58, 47.81, 27.05, 24.03; IR ($CCl_4$)

(26) Dobashi, Y.; Hara, S. *J. Org. Chem.* **1987**, *52*, 2490.

1761, 1732 $cm^{-1}$; HRMS for $C_{11}H_{14}O_5$ ($M^+$) calcd 226.0841, found 226.0842; CIMS *m/z* 227 ($M^+ + 1$, 100).

**Preparation of Ketone 8.** Following the procedure for ketone **6**: from (±)-6,6′-dimethyl-2,2′-diphenic acid[27] (135 mg, 0.5 mmol), 1,3-dihydroxyacetone (67.6 mg, 0.75 mmol), anhydrous $CH_3CN$ (50 mL), triethylamine (0.42 mL, 3.0 mmol), and 2-chloro-1-methylpyridinium iodide (306.6 mg, 1.2 mmol) was obtained ketone **8** (20 mg, 12% yield) as a white solid: analytical TLC (silica gel 60), 30% EtOAc in hexane, $R_f = 0.30$; mp 135−137 °C; $^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 7.48−7.32 (m, 6H), 5.45 (d, $J$ = 15 Hz, 2H), 4.14 (d, $J$ = 15 Hz, 2H), 2.12 (s, 6 H); $^{13}$C NMR (67.94 MHz, $CDCl_3$) $\delta$ 202.31, 167.13, 137.90, 136.31, 132.61, 132.09, 127.72, 124.79, 66.91, 19.80; IR ($CCl_4$) 1759, 1739 $cm^{-1}$; HRMS for $C_{19}H_{16}O_5$ ($M^+$) calcd 324.0998, found 324.0990; CIMS *m/z* 325 ($M^+ + 1$, 100).

**Preparation of Ketone 10.** Following the procedure for ketone **6**: from (±)-6,6′-dinitro-2,2′-diphenic acid[28] (44.5 mg, 0.13 mmol), 1,3-dihydroxyacetone (18 mg, 0.20 mmol), anhydrous $CH_3CN$ (14 mL), triethylamine (0.2 mL, 1.07 mmol), and 2-chloro-1-methylpyridinium iodide (137 mg, 0.54 mmol) was obtained ketone **9** (20 mg, 12% yield) as a pale yellow solid: analytical TLC (silica gel 60), 80% EtOAc in hexane, $R_f = 0.6$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.39 (dd, $J$ = 8.2 Hz, 1.2 Hz, 2H), 7.88 (dd, $J$ = 7.7 Hz, 1.2 Hz, 2H), 7.73 (t, $J$ = 8.0 Hz, 2H), 5.5 (d, $J$ = 15.2 Hz, 2H), 4.21 (d, $J$ = 15.2 Hz, 2H); $^{13}$C NMR (67.94 MHz, $CDCl_3$) $\delta$ 200.20, 164.52, 148.34, 133.70, 132.69, 129.97, 129.68, 127.54, 67.22; IR ($CCl_4$) 1769, 1744, 1543, 1350 $cm^{-1}$; EIMS (20 eV) *m/z* 340 ($M^+ - NO_2$, 100); CIMS *m/z* 387 ($M^+ + 1$, 100).

**Preparation of Ketone 9.** Diphenic acid (121 mg, 0.5 mmol) and 1,3-dihydroxyacetone (67.6 mg, 0.75 mmol) were dissolved in anhydrous $CH_3CN$ (50 mL). Triethylamine (1.1 mL, 8 mmol) was added to the reaction mixture. The resulting solution was stirred at rt for 15 min followed by addition of 2-chloro-1-methylpyridinium iodide (1.02 g, 4 mmol). The reaction mixture was stirred under $N_2$ atmosphere at rt for 12 h and then refluxed for 1 h. The solvent was evaporated off under reduced pressure. The dark-brown residue was diluted with $CH_2Cl_2$. The organic phase was washed twice with $H_2O$, dried over $Na_2SO_4$, filtered, and concentrated. The residue was purified by flash column chromatography: 30 g of silica gel (Merck, 230−400 mesh) in hexane (200 mL) and $Et_3N$ (2 mL) was poured into a column of 30 mm diameter. The column was eluted with hexane followed by 35% EtOAc in hexane to give ketone **9**[8a] (67 mg, 45% yield) as a white solid: analytical TLC (silica gel 60), 30% EtOAc in hexane, $R_f$ = 0.33; mp 166−167 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.43−7.65 (m, 8H), 5.73 (d, $J$ = 15.6 Hz, 2H), 4.23 (d, $J$ = 15.6 Hz, 2H); $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 202.085, 167.21, 138.76, 132.23, 131.57, 130.56, 127.86, 127.24, 66.81; IR ($CCl_4$) 1758, 1737 $cm^{-1}$; HRMS for $C_{17}H_{12}O_5$ ($M^+$) calcd 296.0685, found 296.0683; EIMS (20 eV) *m/z* 296 ($M^+$, 52), 180 (100); CIMS *m/z* 297 ($M^+ + 1$, 7), 296 ($M^+$, 48), 180 (100).

**Preparation of Ketone 7.** 1,1-Cyclohexanediacetic acid (300 mg, 1.5 mmol; azeotroped three times with toluene) and 3-chloro-2-chloromethyl-1-propene (187.5 mg, 1.5 mmol) were dissolved in anhydrous DMF (150 mL). Cesium carbonate (1.08 g, 3.3 mmol) was added to this solution. The resulting mixture was stirred at 95 °C under $N_2$ atmosphere for 10 h. The reaction mixture was diluted with EtOAc and washed four times with water. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography (20% EtOAc in hexane) to give compound **7b** (253 mg, 67% yield) as a white solid: analytical TLC (silica gel 60), 30% EtOAc in hexane, $R_f = 0.6$; mp 54−55 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.29 (s, 2H), 4.77 (s, 4H), 2.38 (s, 4H), 1.61−1.44 (m, 10H); $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 171.67, 137.98, 120.44, 66.69, 44.07, 37.48, 37.19, 25.81, 21.60; IR ($CH_2Cl_2$) 1737 $cm^{-1}$; HRMS for $C_{14}H_{20}O_4$ ($M^+$) calcd 252.1362, found 252.1359.

A stock solution of ruthenium trichloride hydrate (843 mg, 4 mmol) in water (100 mL) was prepared. Compound **7b** (50.4 mg, 0.2 mmol) was dissolved in $CH_3CN$ (3 mL) and water (2 mL). The stock solution (0.2 mL) was transferred to the reaction mixture. To this mixture was added, in portions, a mixture of Oxone (307 mg, 0.5 mol) and sodium bicarbonate (130 mg, 1.55 mol) over a period of 30 min at rt. The reaction was complete in 40 min as shown by TLC. The reaction mixture was diluted with EtOAc and washed twice with brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by flash column chromatography: 30 g of silica gel (Merck, 230−400 mesh) in hexane (200 mL) and $Et_3N$ (2 mL) was poured into a column of 30 mm diameter. The column was eluted with hexane, followed by 35% EtOAc in hexane to give ketone **7** (46.1 mg, 90%) as a colorless oil: analytical TLC (silica gel 60), 30% EtOAc in hexane, $R_f = 0.3$; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.76 (s, 4H), 2.49 (s, 4H), 1.70−1.40 (m, 10H); $^{13}$C NMR (67.94 MHz, $CDCl_3$) 201.80, 171.01, 68.03, 42.97, 37.68, 36.53, 25.66, 21.56; IR ($CCl_4$) 1755 $cm^{-1}$; HRMS for $C_{13}H_{18}O_5$ ($M^+$) calcd for 254.1154, found 254.1152; EIMS (20 eV) *m/z* 254 ($M^+$, 9), 94 (100).

**Preparation of Ketone 9.** Following the procedure for compound **7b**: from diphenic acid (606 mg, 2.5 mmol), 3-chloro-2-chloromethyl-1-propene (313 mg, 2.5 mmol), anhydrous DMF (200 mL), and cesium carbonate (1.8 g, 5.5 mmol), at 95 °C for 24 h, was obtained compound **9b** (409 mg, 56% yield) as a white solid: analytical TLC (silica gel 60), 20% EtOAc in hexane, $R_f = 0.5$; mp 240−241 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.59−7.38 (m, 8H), 5.66 (d, $J$ = 14.2 Hz, 2H), 5.20 (s, 2H), 4.41 (d, $J$ = 14.2 Hz, 2H); $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 168.37, 140.22, 138.97, 133.15, 130.94, 130.52, 127.62, 126.93, 114.19, 64.60; IR ($CCl_4$) 1752 $cm^{-1}$; HRMS for $C_{18}H_{14}O_4$ ($M^+$) calcd 294.0892, found 294.0893; EIMS (20 eV) *m/z* 294 ($M^+$, 100). Following the cleavage procedure for ketone **7**: from compound **9b** (58.8 mg, 0.2 mmol) was obtained ketone **9** (49.7 mg, 84% yield) as a white solid.

**General *in Situ* Epoxidation Procedure. Preparation of *trans*-Stilbene Epoxide (Entry 9, Table 1).** To an $CH_3CN$ solution (1.5 mL) of *trans*-stilbene (18 mg, 0.1 mmol) and cyclic ketone **9** (29.6 mg, 0.1 mmol) at rt was added an aqueous $Na_2$·EDTA solution (1 mL, $4 \times 10^{-4}$ M). To this mixture was added, in portions, a mixture of Oxone (246 mg, 0.4 mmol) and sodium bicarbonate (104 mg, 1.24 mmol). The reaction was complete in 7 min at rt as shown by TLC. The reaction mixture was poured into water and extracted three times with $CH_2Cl_2$. The organic layer was dried over anhydrous $Na_2SO_4$. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography: 20 g of silica gel (Merck, 230−400 mesh) in hexane (100 mL) and $Et_3N$ (1 mL) was poured into a column of 20 mm diameter. The column was eluted with hexane, followed by 5% EtOAc in hexane to give *trans*-stilbene epoxide (19.6 mg, 99% yield), and with 35% EtOAc in hexane to recover ketone **9** (28.4 mg, 93% recovery).

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**Supporting Information Available:** Determination of the hydration equilibrium constants for ketones **3** and **6**−**10**,

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(28) Synthesis of (±)-6,6′-dinitro-2,2′-diphenic acid was carried out according to the literature procedures, see: (a) Whitmore, F. C.; Culhane, P. J.; Neher, H. T. *Organic Syntheses*; Wiley & Sons: New York, 1976; Collect Vol. I, 56. (b) Culhane, P. J. *Organic Syntheses*, Wiley & Sons: New York, 1976; Collect Vol. I, 125.

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$^{1}H$ and $^{13}C$ NMR spectra for ketones **4**−**10**, **7b**, and **9b**, and X-ray structural analyses of ketones **5** and **9** containing tables of atomic coordinates, thermal parameters, bond lengths, and angles (33 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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