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A Highly Efficient Ruthenium-Catalyzed Rearrangement of α,β-Epoxyketones to 1,2-Diketones

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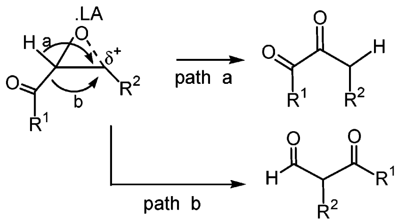
$TpRuPPh_3(CH_3CN)_2PF_6$ catalyzed the efficient rearrangement of α,β-epoxyketones to 1,2-diketones. Unlike a previously reported iron catalyst, the reaction in this case is applicable not only to 1,2-disubstituted epoxides but also to mono- and trisubstituted epoxides and tolerates oxygen functionalities. The sterically crowded and highly basic tris(1-pyrazolyl)borate (Tp) ligand of the ruthenium catalyst might account for its high selectivity toward 1,2-diketone rather than 1,3-diketone.

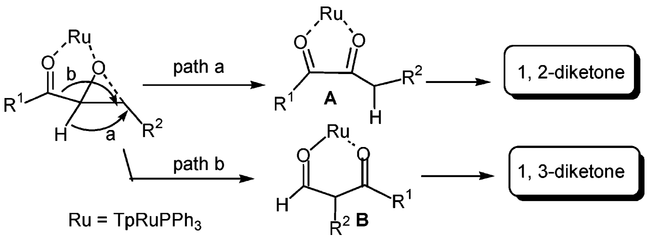
Introduction

The rearrangement of epoxides by Lewis acids is an important method for obtaining organic ketones or aldehydes.[1,2] The rearrangement of α,β-epoxyketones by a Lewis acid was reported by House in the early 1960s;[1] the products normally consist of a mixture of 1,2- and 1,3-diketones, which result from either hydride or acyl migration, respectively.[2] In most cases, acyl migration is the preferred pathway because it shows neighboring group participation in opening of the epoxide ring.[2] The selective formation of 1,2- or 1,3-diketone from α,β-epoxyketones is an interesting issue in organic synthesis.[1−9] Several methods have been developed for selective synthesis of 1,3-diketones using acid or metal catalysts such as $BF_3{\cdot}Et_2O$,[2c,d,3] $LiClO_4$,[4] zeolites,[5] and $Pd(PPh_3)_4$.[6] In contrast, little is known about the selective synthesis of 1,2-diketones due to slow hydride migration (path A, Scheme 1). Although $Mg(ClO_4)_2$[2a] and $Ti(O^i\text{-}Pr)_2Cl_2$[7] are selective for the synthesis of 1,2-diketone, an excess of acid (>1.0 equimolar) is required. Silica gel shows activity for the rearrangement of chalcone epoxides to 1,2-diketones, but the reaction only works for derivatives of chalcone epoxides.[8] Suda reported that an iron-porphyrin catalyst effected the selective synthesis of 1,2-diketones,[9] but the examples are limited to only 1,2-disubstituted epoxyketones. In this report, we describe a new ruthenium catalytic reaction that is applicable not only to 1,2-disubstituted α,β-epoxyketones but also to mono- and trisubstituted analogues. The trend in the catalytic activity of these epoxides is opposite that observed for common acid catalysts.[2−5]

SCHEME 1



SCHEME 2



Results and Discussions

Scheme 2 shows the working hypothesis regarding the use of $TpRuPPh_3(CH_3CN)_2{-}PF_6$[10] catalyst to enhance the desired 1,2-hydrogen shift (path a). This cationic catalyst contains two labile CH_3CN, a sterically crowded tris(1-pyrazolyl)borate, and one triphenylphosphine ligand. This structural feature is more suitable for the formation of five-membered chelated diketone **A** rather than the six-membered chelated species **B**. The bulky size of

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[1] (a) House, H. O. *J. Am. Chem. Soc.* **1954**, *76*, 1235. (b) House, H. O.; Ryerson, G. D. *J. Am. Chem. Soc.* **1961**, *83*, 979.

[2] (a) Klix, R. C.; Bach, R. D. *J. Org. Chem.* **1987**, *52*, 580. (b) Bach, R. D.; Klix, R. C. *J. Org. Chem.* **1985**, *50*, 5440. (c) Bach, R. D.; Domagala, J. M. *J. Org. Chem.* **1984**, *49*, 4181. (d) Bach, R. D.; Klix, R. C. *Tetrahedron Lett.* **1985**, *26*, 985.

[3] (a) Kunisch, F.; Hobert, K.; Welzel, P. *Tetrahedron Lett.* **1985**, *26*, 6039. (b) Okuda, K.; Katsura, T.; Tanino, H.; Kakoi, H.; Inoue, S. *Chem. Lett.* **1994**, 157.

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[5] Elings, J. A.; Lempers, H. E. B.; Sheldon, R. A. *Eur. J. Org. Chem.* **2000**, *10*, 1905.

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[10] Chan, W.-C.; Lau, C.-P.; Chen, Y.-Z.; Fang, Y.-Q.; Ng, S.-M.; Jia, G. *Organometallics* **1997**, *16*, 34.

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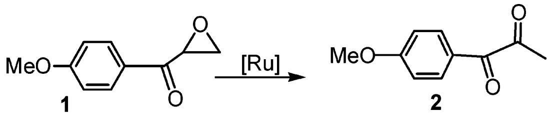
TABLE 1. Catalytic Transformation over Various Solvents and Catalysts



[Ru] = $TpRuPPh_3(CH_3CN)_2PF_6$

entry	catalyst	solvent	conditions	yields[b] (recovery)[c]
1	$TpRuPPh_3(CH_3CN)_2PF_6$	toluene	100 °C (5 h)	99%
2	$TpRuPPh_3(CH_3CN)_2PF_6$	CH_3CN	85 °C (12 h)	94%
3	$TpRuPPh_3(CH_3CN)_2PF_6$	DME	85 °C (12 h)	87% (10%)
4	$TpRuPPh_3(CH_3CN)_2PF_6$	DCE	80 °C (12 h)	71% (23%)
5	$TpRuPPh_3(CH_3CN)_2PF_6$	benzene	80 °C (12 h)	81% (17%)
6	$TpRuPPh_3(CH_3CN)_2PF_6$	DMF	110 °C (6 h)	89% (9%)
7	$TpRu(PPh_3)_2Cl$	toluene	100 °C (5 h)	90%
8	$CpRu(PPh_3)_2Cl$	toluene	100 °C (5 h)	(94%)
9	$CpRu(PPh_3)(CH_3CN)_2PF_6$	toluene	100 °C (5 h)	(5%)

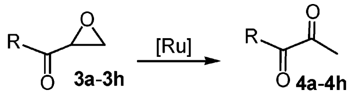
[a] Performed with 10 mol % catalyst, [substrate] = 0.80 M. [b] Products were isolated from silica column. [c] Values in parentheses represent recovery yields of compound **1**.

structure **B** is less compatible with the congested space around the ruthenium center. This catalyst has catalytic activity toward transfer hydrogenation[11] and cleavage of a carbon–carbon triple bond.[12]

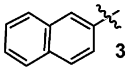
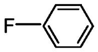
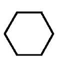
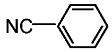
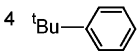
We examined the isomerization of monosubstituted epoxide **1** in various solvents, and the results are shown in Table 1. The yield of diketone **2** is quantitative with 10 mol % $TpRuPPh_3(CH_3CN)_2PF_6$ in hot toluene (100 °C, 5 h) and remains as high as 93% if 5 mol % catalyst is used (toluene, 100 °C, 10 h). Other solvents are also effective (entries 2–6) and give diketones **2** in yields of 71–94% without the formation of byproducts including 1,3-diketone, and this condition might be reflected by the recovery yields of α,β-epoxyketone **1** in dimethoxyethane (10%), dichloroethane (23%), benzene (17%), and dimethylformamide (9%). We examined three other catalysts (entries 7–9) to assess the effect of the tris(1-pyrazolyl)borate and triphenyl phosphine ligands. To our surprise, a slight decrease in the yield (90%) of 1,2-diketone **1** was observed for $TpRu(PPh_3)_2Cl$. This result is attributed to a rapid dissociation of PPh_3 in the presence of bulky tris(1-pyrazolyl)borate ligand.[10] The replacement of tris(1-pyrazolyl)borate ligand with a cyclopentadienyl group, as in $CpRu(PPh_3)(CH_3CN)_2PF_6$,[13] led to catalytic inactivity with exclusive recovery of the starting epoxyketone **1** (>94%). This phenomenon is unexpected because the metal is more acidic for $CpRu(PPh_3)(CH_3CN)_2PF_6$ than for $TpRu(PPh_3)(CH_3CN)_2PF_6$.

The rearrangement of monosubstituted α,β-epoxyketones such as **1** normally gave complicated mixtures of products with a conventional acidic catalyst like $BF_3\cdot Et_2O$.[9] It is unfavorable to produce carbocation character on the CH_2 terminus during the ring-opening of epoxide. The ease and excellent yields in the rearrangement of α,β-epoxyketone **1** with $TpRuPPh_3(CH_3CN)_2PF_6$ catalyst encouraged us to perform an extensive investigation. Table 2 shows the suitability of this catalyst with various monosubstituted α,β-epoxy ketones. The ketone substrates include phenyl and its 4-substituted fluoro, cyano, and *tert*-butyl substituents (entries 1–4), with yields exceeding 92%. It is also applicable to 2-naphthyl, cyclohexyl, and *n*-octyl groups (entries 5–7) without the formation of byproducts including 1,3-diketones. A reaction period of 5 h is sufficient to complete the isomerization of these substrates (toluene, 100 °C).

TABLE 2. Catalytic Transformation of Various Monosubstituted Epoxides



[Ru]=$TpRuPPh_3(CH_3CN)_2PF_6$

entries	R (epoxides)		Product (yields)	entries	R (epoxides)		Product (yields)
1		**3a**	**4a** (93%)	5		**3e**	**4e** (97%)
2		**3b**	**4b** (95%)	6		**3f**	**4f** (98%)
3		**3c**	**4c** (92%)	7	C_8H_{17}	**3g**	**4g** (93%)
4		**3d**	**4d** (95%)				

[a] Conditions: 10 mol % catalyst, [substrate] = 0.80 M, 100 °C, 5 h. [b] Products were isolated from silica column.

In contrast to monosubstituted epoxides, rearrangement of 1,2-disubstituted α,β-epoxy ketones requires a greater duration of reaction (toluene, 100 °C, 12 h) to complete the catalytic reaction (Table 3). This catalytic reaction is equally effective for both *trans*- and *cis*-epoxides **5a** and **5b**, respectively. The isolated yields of the corresponding 1,2-diketones were as high as 91–94% (Table 3, entries 1–2). Entries 3–8 show various α,β-epoxyketones **5c–h** with a change in the R^1 and R^3 substituents, which gave 1,2-diketones **6c–h** in excellent yields (>90%) without the formation of 1,3-diketones or other byproducts. To our surprise, the styryl epoxide **5i** (entry 9) failed to undergo rearrangement, and was recovered in 91% yield. Epoxide **5i** is expected to be more reactive than analogues with alkyl substituents (**5c–h**) if carbocation character is developed during the opening of epoxides.[1–8] We also prepared trisubstituted epoxyketones **5j** and **5k** (entries 10 and 11) that also efficiently gave 1,2-diketones **6j** and **6k**, but the reaction time was as long as 18 h. The relative activities of these epoxides

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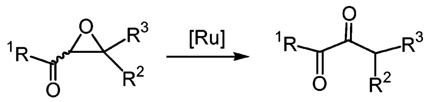
[11] Yeh, K.-L.; Liu, B.; Lo, C.-Y.; Liu, R.-S. *J. Am. Chem. Soc.* **2002**, *124*, 6510.

[12] Datta, S.; Chang, C.-L.; Yeh, K.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **2003**, *125*, 9294.

TABLE 3. Rearrangement of Di- and Trisubstituted Epoxyketones

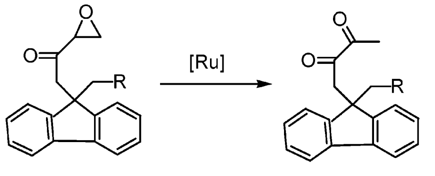


[Ru]=TpRuPPh$_3$(CH$_3$CN)$_2$PF$_6$

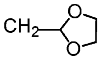
entries	epoxides	R^1	R^2	R^3	product (yields)
1	**5a**	Ph	*cis*-H	*trans*-^{n}C$_4$H$_9$	**6a** (94%)
2	**5b**	Ph	*cis*-^{n}C$_6$H$_{13}$	*trans*-H	**6b** (91%)
3	**5c**	Ph	H	Me	**6c** (93%)
4	**5d**	2-naphthyl	H	Me	**6d** (94%)
5	**5e**	cyclohexyl	H	Me	**6e** (92%)
6	**5f**	^{n}C$_8$H$_{17}$	*cis*-H	*trans*-^{n}Cu	**6f** (95%)
7	**5g**	^{i}Pr	*cis*-H	*trans*-^{n}C$_6$H$_{13}$	**6g** (90%)
8	**5h**	^{t}Bu	*cis*-H	*trans*-^{n}Bu	**6h** (90%)
9	**5i**	^{n}C$_6$H$_{13}$	H	Ph	nr[c]
10	**5j**	Ph	Me	Me	**6j** (95%)
11	**5k**	^{n}C$_{14}$H$_{29}$	Me	Me	**6k** (90%)

[a] Conditions: 10 mol % catalyst, [substrate] = 0.80 M, 100 °C, 12 h for entries 1−8, 18 h for entries 9−11. [b] Products were isolated from silica column. [c] Recovery yield of **5i** was 91% in this case.

SCHEME 3[a]



[Ru] = TpRuPPh$_3$(CH$_3$CN)$_2$PF$_6$

entries	R	epoxides	products (yields)
1	CHO	**7a**	**8a** (86 %)
2	CH$_2$OH	**7b**	**8b** (81 %)
3		**7c**	**8c** (89%)
4	CH =CH$_2$	**7d**	**8d** (91 %)
5	*cis*-CH =CH(^{n}Pr)	**7e**	**8e** (90 %)

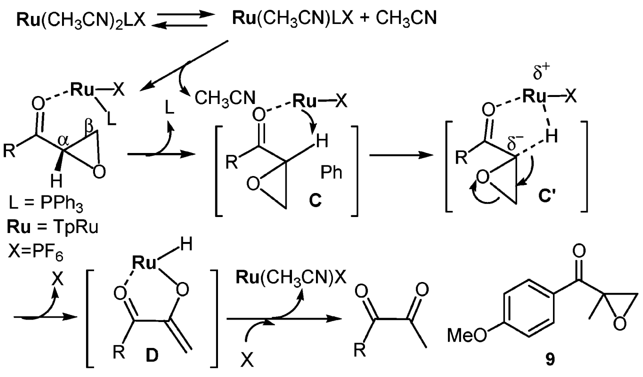
[a] Conditions: 10 mol % catalyst, [substrate] = 0.80 M, 100 °C, 8 h. [b]Products were isolated from silica column.

decrease in the order monosubstituted > 1,1-disubstituted > trisubstituted epoxides.

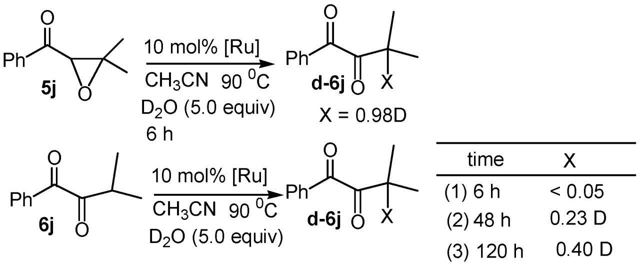
We also examined the ability of this catalytic activity to tolerate different functional groups. As shown in Scheme 3, we prepared various monosubstituted α,*β*-epoxyketones **7a**−**e** bearing an aldehyde, alcohol, dioxalane, mono-, and 1,2-disubstituted alkenes. The 1,2-diketones **8a**−**e** were isolated in yields of 81−91%, which indicates that this catalytic reaction is applicable to various oxygen functionalities. The alkene product **8e** retains a cis geometry without isomerization of the olefin functionality.

Scheme 4 shows a plausible mechanism that is distinct from those observed for acid catalysts.[1−8] The active ruthenium species are likely to be neutral TpRuPPh$_3$(CH$_3$CN)PF$_6$ in toluene because TpRu(PPh$_3$)$_2$Cl is equally active. Acid-promoted ring opening of the epoxides seems unlikely for the present system. The catalytic inactivity of styryl oxide **5i** indicates that neither benzyl carbocation nor radical character is being developed in this reaction mechanism. We propose that the ruthenium complex coordinates with the carbonyl group of α,*β*-epoxyketone to generate species **C**. The approach of the ruthenium center to the acidic C$_\alpha$-proton develops carboanion character to induce ring opening of the epoxides, giving five-membered chelated enolate anion **D**. Reprotonation of the enolate functionality with the Ru−H bond of species **D** is expected to regenerate active ruthenium species and 1,2-diketone product. To examine this hypothesis, we prepared the substrate **9**, which was found to be inactive in hot toluene using TpRuPPh$_3$(CH$_3$CN)$_2$PF$_6$ catalyst (100 °C, 12 h) with a 90% recovery. The catalytic inactivity of compound **9** is attributed to the lack of a C$_\alpha$-proton. Scheme 5 shows a crucial experiment to confirm the enolate intermediate **D**. We selected epoxide **5j** as a molecule for study because the resulting product **6j** has a less acidic isopropyl proton to retard proton exchange with external D$_2$O. In the presence of D$_2$O, treatment of epoxide **5j** with 10 mol % ruthenium catalyst in hot CH$_3$CN (90 °C, 6 h) gave product **6j** containing 98% deuterium content, which is thought to derive from protonation of enolate species **D** with D$_2$O. The proton exchange of product **6j** with external D$_2$O proved to be too slow to account for such a large deuterium content on the basis of a blank experiment.

SCHEME 4



SCHEME 5



time	X
(1) 6 h	< 0.05
(2) 48 h	0.23 D
(3) 120 h	0.40 D

Conclusion

We have developed a catalytic reaction for the efficient rearrangement of α,*β*-epoxyketones to 1,2-diketones. The substrates include monosubstituted, 1,2-disubstituted, and trisubstituted α,*β*-epoxy ketones. The trend in the catalytic activity of these epoxides is opposite that seen with common acid catalysts. This catalytic reaction tolerates suitable oxygen functionalities. 1,2-Diketones are recognized as versatile intermediates in organic synthesis, and their synthesis has received considerable attention.[14,15] The present method appears to be useful in view of its simplicity (no additives), high yields, and wider range of suitable α,β-epoxyketones. Detailed studies are underway to elucidate the reaction mechanism.[16]

Experimental Section

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere in oven-dried glassware using a standard syringe, cannula, and septa apparatus. Benzene, diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane was dried over CaH_2 and distilled before use. Vinylmagnesium bromide, *p*-methoxyphenyl aldehyde, *m*-chloroperbenzoic acid, and tetra-*n*-propylammonium perruthenate (TPAP) were obtained commercially and used without purification. $TpRu(PPh_3)(CH_3CN)_2PF_6$ was prepared by heating $TpRu(PPh_3)_2Cl$ with $LiPF_6$ in CH_3CN according to a literature method.[10] Spectral data of compounds **3a**–**h**, **4a**–**h**, **5a**–**k**, **6a**–**k**, and **7a**–**e** in repetitive experiments are provided in Supporting Information.

(1) Standard Procedure for the Synthesis of α,β-Epoxyketone. Synthesis of 1-(4-Methoxy-phenyl)-prop-2-en-1-ol. To a THF (10 mL) solution of *p*-methoxyphenyl aldehyde (2.00 g, 14.7 mmol) was added vinylmagnesium bromide (17.6 mL, 1 M, 17.6 mmol) at 0 °C, and the mixture was stirred for 2 h before addition of H_2O. The solution was evaporated under reduced pressure, and the organic layer was extracted with diethyl ether. The extract was dried in vacuo and chromatographed through a silica column to give allylic alcohol as a colorless oil (1.98 g, 12.0 mmol, 82%). IR (neat, cm^{-1}): 3423 (vs, br), 1645 (m), 1614 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.28 (d. $J = 8.8$ Hz, 2H), 6.87 (d, $J = 8.8$ Hz, 2H), 6.07–5.99 (m, 1H), 5.33 (dd, $J = 17.6, 1.5$ Hz, 1H), 5.16 (dd, $J = 12.8, 1.5$ Hz), 5.14 (s, 1H), 3.78 (s, 3H), 1.94 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 140.3, 134.8, 127.6, 114.6, 113.8, 74.7, 55.2. HRMS (70 eV): calcd for $C_{10}H_{12}O_2$, 164.0837; found, 164.0836.

(2) Synthesis of (4-Methoxy-phenyl)-oxiranyl-methanone (1). To a CH_2Cl_2 solution (20 mL) of the preceding alcohol (1.20 g, 7.31 mmol) was added *m*-chloroperbenzoic acid (2.52 g, 14.6 mmol), and the mixture was stirred at 26 °C for 12 h before addition of water (10 mL). The organic layer was extracted with diethyl ether, washed with $NaHCO_3$ solution, and dried over $MgSO_4$. The extract was concentrated and eluted through a silica (hexane/$NEt_3 = 100/1$) column to give an epoxide as a colorless oil (1.20 g, 6.66 mmol). To a CH_2Cl_2 solution (20 mL) was added the epoxide (1.20 g, 6.66 mmol), *N*-methyl morpholine oxide (1.35 g, 10.0 mmol), TPAP (117 mg, 0.33 mmol), and powdered 4 Å molecular sieves (0.50 g), and the mixture was stirred at 25 °C for 1 h. The mixture was filtered, dried in vacuo, and chromatographed through a short alumina column to afford α,β-epoxyketone **1** (1.05 g, 5.92 mmol, 81%) as a colorless oil. $R_f = 0.41$ (ether/hexane = 1/3). IR (neat, cm^{-1}): 3032 (w), 1722 (s), 1622 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, $J = 8.4$ Hz, 2H), 6.95 (d, $J = 8.4$ Hz, 2H), 4.18 (t, $J = 2.6$ Hz, 1H), 3.87 (s, 3H), 3.06 (t, $J = 2.6$ Hz, 1H), 2.96–2.93 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8, 164.0, 130.5, 128.3, 113.9, 55.3, 50.6, 47.2. HRMS: calcd for $C_{10}H_{10}O_3$, 178.0630; found, 178.0632.

(3) Procedure for Catalytic Reactions. To a toluene solution (0.70 mL) were added epoxide **1** (100 mg, 0.56 mmol) and $TpRuPPh_3(CH_3CN)_2PF_6$ (43 mg, 0.056 mmol), and the reaction mixture was heated at 100 °C for 5 h. The solution was filtered over a short silica bed and then washed with diethyl ether (4 mL). Concentration of the filtrate under reduced pressure gave 1,2-diketone **2** as a yellow oil (99 mg, 0.55 mmol, 99%).

(4) 1-(4-Methoxy-phenyl)-propane-1,2-dione (2). $R_f = 0.59$ (ether/heaxane = 1/3); IR (neat, cm^{-1}): 3031 (w), 1732 (s), 1720 (s), 1622 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, $J = 8.4$ Hz, 2H), 6.94 (d, $J = 8.4$ Hz, 2H), 3.87 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 189.9, 164.7, 132.7, 124.6, 114.1, 55.5, 26.4. HMRS: calcd for $C_{10}H_{10}O_3$, 178.0630; found, 178.0631.

(5) Oxiranyl-phenyl-methanone (3a). This epoxide was prepared similarly from vinylmagnesium bromide and benzaldehyde, followed by sequential epoxidation with *m*-chloroperbenzoic acid and oxidation with TPAP according to the synthetic procedure for compound **1**. $R_f = 0.52$ (ether/hexane = 1/3). IR (neat, cm^{-1}): 3033 (w), 1717 (s), 1619 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, $J = 7.2$ Hz, 2 H), 7.58 (t, $J = 7.2$ Hz, 1 H), 7.48 (t, $J = 7.2$ Hz, 2 H), 4.22 (dd, $J = 4.4, 2.4$ Hz, 1 H), 3.10 (dd, $J = 6.4, 4.4$ Hz, 1 H), 2.95 (dd, $J = 6.4, 4.4$ Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 194.5, 135.3, 133.8, 128.7, 128.2, 50.9, 47.4. HMRS: calcd for $C_9H_8O_2$, 148.0524; found, 148.0526.

(6) 1-Phenyl-propane-1,2-dione (4a). This diketone was obtained similarly from heating epoxide **3a** with ruthenium catalyst in hot toluene (100 °C, 5 h) according to the procedure for compound **2**. $R_f = 0.57$ (ether/hexane = 1/3). IR (neat, cm^{-1}): 3035 (w), 1716 (s), 1617 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, $J = 7.6$ Hz, 2 H), 7.62 (t, $J = 7.6$ Hz, 1 H), 7.48 (t, $J = 7.6$ Hz, 2 H), 2.51 (s, 3 H). ^{13}C NMR (125 MHz $CDCl_3$): δ 200.5, 191.3, 134.5, 131.7, 130.2, 128.8, 26.3. HMRS: calcd for $C_{10}H_{10}O_2$, 148.0524; found, 148.0525.

(7) 3-(*E*)-Butyl-oxiranyl-phenyl-methanone (5a). This epoxide was prepared similarly from 1-hexenylmagnesium bromide and benzaldehyde, followed by sequential epoxidation with *m*-chloroperbenzoic acid and oxidation with TPAP according to the synthetic procedure for compound **1.** $R_f = 0.51$ (ether/hexane = 1/3). IR (neat, cm^{-1}): 3034 (w), 1720 (s), 1622 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, $J = 7.3$ Hz, 2H), 7.60 (t, $J = 7.3$ Hz, 1H), 7.48 (t, $J = 7.3$ Hz, 2H), 4.00 (d, $J = 2.0$ Hz, 1H), 3.14–3.10 (m, 1H), 1.77–1.66 (m, 2H), 1.52–1.46 (m, 2H), 1.44–1.36 (m, 2H), 0.91 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.5, 135.4, 133.6, 128.6, 128.1, 59.9, 57.2, 31.5, 27.2, 22.2, 13.7. HMRS: calcd for $C_{13}H_{16}O_2$, 204.1150; found, 204.1153.

1-Phenyl-heptane-1,2-dione (6a). This diketone was obtained similarly from heating epoxide **5a** with ruthenium catalyst in hot toluene (100 °C, 10 h) according to the procedure for compound **2**. $R_f = 0.75$ (ether/hexane = 1/3). IR (neat, cm^{-1}): 3037 (w), 1735 (s), 1712 (s), 1618 (w). ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, $J = 7.8$ Hz, 2H), 7.64 (t, $J = 7.8$ Hz, 1H), 7.50 (t, $J = 7.8$ Hz, 2H), 2.87 (t, $J = 7.4$ Hz, 2H), 1.72–1.70 (m, 2H), 1.38–1.32 (m, 4H), 0.90 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.4, 192.5, 134.4, 131.9, 130.0, 128.7, 38.6, 31.2, 22.4, 22.3, 13.8. HMRS: calcd for $C_{13}H_{16}O_2$, 204.1150; found, 204.1151.

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Supporting Information Available: Spectral data of α,β-epoxyketones **3b**–**g**, **5b**–**k**, and **7a**–**e** and 1,2-diketones **4b**–**h**, **6b**–**k**, and **8a**–**e** in repetitive experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) $CpRu(CH_3CN)_2PPh_3PF_6$ was prepared in situ from equimolar of $CpRu(CH_3CN)_3PF_6$ and PPh_3.

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(16) Mechanism of this rearrangement is also distinct from that of the iron-porphyrin catalyst,[9] which is applicable to styrylepoxy ketones **5i**, affording excellent yields of 1,2-diketone products.

(17) Although this catalytic reaction works well for α,β-epoxy ketones, it is not applicable to α,β-epoxy aldehydes.