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Metal-Free Dihydroxylation of Alkenes using Cyclobutane Malonoyl Peroxide

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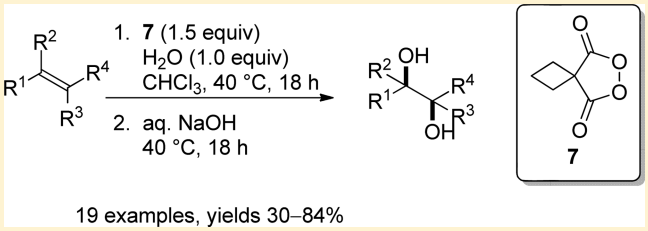
Supporting Information

ABSTRACT: Cyclobutane malonoyl peroxide (**7**), prepared in a single step from the commercially available diacid **6**, is an effective reagent for the dihydroxylation of alkenes. Reaction of a chloroform solution of **7** with an alkene in the presence of 1 equiv of water at 40 °C followed by alkaline hydrolysis leads to the corresponding diol (30−84%). With 1,2-disubstituted alkenes, the reaction proceeds with *syn*-selectivity (3:1 → 50:1). A mechanism consistent with experimental findings is proposed, which is supported by deuterium and oxygen labeling studies and explains the stereoselectivity observed. Alternative reaction pathways that are dependent on the structure of the starting alkene are also described leading to the synthesis of allylic alcohols and γ-lactones.



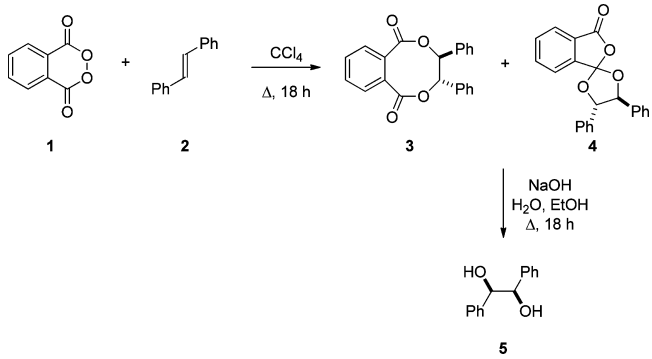
INTRODUCTION

Over the past decade, metal-free transformations have been driven to the forefront of chemical research. Transition metals enjoy widespread use in organic synthesis;[1] however, the cost, toxicity, and environmental impact of many of these reagents/catalysts have made their use increasingly prohibitive. In general, metal-free reactions offer a number of notable advantages, including the fact they are often inexpensive and the reagents are easy to prepare, bench-stable, tolerant of moisture and air, and nontoxic. It is for these reasons that the development of metal-free methods continues to attract significant research interest.

Oxidation is central to synthetic chemistry.[2] The chemical industry relies on the selective oxidation of hydrocarbon feedstocks in the production of numerous commodity materials, which find application in all areas of life.[3] From a synthetic standpoint, oxidation is used extensively in the formation of fine chemicals and natural products.[4] Owing to its importance, a staggering number of reagents and catalytic systems have been developed to promote oxidation.[5] Of the known oxidation methods, alkene dihydroxylation is particularly important. Among the reagents available for alkene dihydroxylation, none have achieved more success than osmium tetroxide.[6] For over eighty years, the use of OsO_4 has been developed and refined, forming the basis of one of the most powerful transformations in synthetic chemistry: the Sharpless asymmetric dihydroxylation (SAD).[7] Despite this reaction's widespread popularity, the toxicity of osmium and high levels of inorganic waste are commonly cited limitations,[8] which has prompted the development of a number of alternative metal catalysts,[9] including palladium,[10] iron,[11] ruthenium,[12] manganese,[13] and copper[14] systems.[15] Metal-free methods for *syn*-dihydroxylation have been reported; however, this area is considerably less established than their metal-based counterparts.[16−18] To date, the development of an asymmetric, metal-free method for the *syn*-dihydroxylation of alkenes remains an elusive and attractive target.

In a series of largely neglected reports, Greene described the synthesis[19] and reactivity[20] of phthaloyl peroxide (PPO) **1**. Within these articles, Greene showed that PPO (**1**) reacts with *trans*-stilbene **2** (CCl_4, 80 °C) to give two dioxygenated products **3** and **4** in a 1:3 ratio (Scheme 1).[20b] Alkaline hydrolysis of **3** and **4** (either separately or as a mixture) leads to (±)-hydrobenzoin **5**.[21] Importantly, it was shown that starting

Scheme 1. Reaction of Phthaloyl Peroxide 1 with *trans*-Stilbene 2



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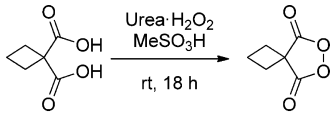
with either *trans*- or *cis*-stilbene, the reaction was stereospecific, formally leading to (±)-hydrobenzoin **5** or *meso*-hydrobenzoin, respectively. Although the overall process was low-yielding, this represents a transition-metal-free *syn*-dihydroxylation with great potential. A recent report from Siegel showed improved reactivity for the derivative 3,4-dichlorophthaloyl peroxide, albeit with reduced stereoselectivities, showing great capacity for further development.[22]

PPO (**1**) is *very* sensitive to shock and explodes at 130 °C, providing an explanation why this interesting transformation has not been significantly developed further. We reasoned that stable cyclic acyl peroxides may provide the basis of a metal-free dihydroxylation procedure, and we have shown that cyclopropane malonoyl peroxide is an effective reagent for alkene *syn*-dihydroxylation.[23] During the development of this reaction, the reactivity of cyclobutane malonoyl peroxide **7** was extensively examined. We now wish to provide a more complete description of the use of **7** for alkene dihydroxylation and highlight alternative reaction pathways that lead to the synthesis of allylic alcohol and γ-lactone products, which are dependent on the structure of the starting alkene.

RESULTS AND DISCUSSION

Cyclobutane malonoyl peroxide **7** was prepared in one step from the commercially available diacid **6** (Scheme 2). A series

Scheme 2. Synthesis of Cyclobutane Malonoyl Peroxide 7



6 **7**

of peroxide sources were examined for this procedure on the basis of existing literature methods, which were restricted to small-scale preparation owing to the use of concentrated hydrogen peroxide solutions[24] or incompatible reagents.[25] The optimized procedure involved treatment of **6** with urea hydrogen peroxide complex,[26] using methane sulfonic acid as an activator and dehydrating agent.[27] Crucially, the reaction could be performed on a reasonable scale (4 g) and conveniently purified by aqueous workup and crystallization.

With an efficient route for the preparation of cyclobutane malonoyl peroxide **7**, we turned our attention to examining its reactivity with alkenes. A set of exploratory investigations revealed that **7** reacts with 4-methylstyrene (**8**) to give two major products **9** and **10** after 18 h (Scheme 3). Treatment of the crude reaction mixture with aqueous sodium hydroxide gave diol **11** in low yield (~30%).

Several important features of this reaction require further discussion. The reaction proceeded under mild conditions in the presence of air and moisture at a temperature considerably lower than that reported by Greene for the reactions of phthaloyl peroxide with alkenes. Cyclobutane carboxylic acid, formed during hydrolysis of **9** and **10**, was removed by aqueous workup facilitating isolation of the diol product. The combination of easily handled reagent and mild conditions made this reaction extremely simple to perform.

Encouraged by this initial discovery, the reaction conditions were optimized with respect to peroxide stoichiometry and solvent (Table 1). Capricious yields were observed using bench acetonitrile, which suggested that the water content of the solvent may have an effect on the reactivity (Table 1, entry 1). Further investigation showed that the use of dry acetonitrile led to a lower isolated yield over 18 h (20% after hydrolysis), whereas the addition of 1 equiv of water to the reaction solvent consistently delivered the diol product in moderate yield (55%) (Table 1, entries 2 and 3), confirming that the presence of water was important to the overall reaction.

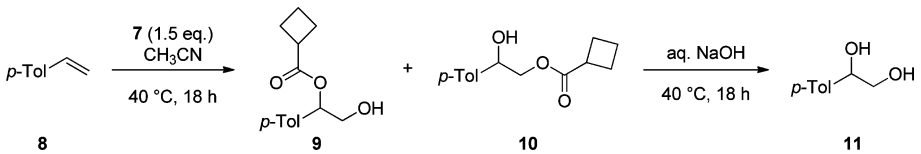
A screen of common reaction solvents revealed that chloroform was the most effective, providing the dihydroxylated product **11** in 69% yield (Table 1, entry 4). On the basis of the water dependency described above, it is interesting that the heterogeneous reaction mixture of chloroform and water delivered the product in higher yield than those of water miscible solvents such as acetonitrile (55%; Table 1, entry 3) and THF (30%; Table 1, entry 5).

The results in Table 1 revealed a strong trend between peroxide equivalents and isolated yield of **11**. Use of excess peroxide led to a sharp decrease in the isolated yield of **11** (Table 1, entries 10 and 11). Use of a slight excess of the reagent (Table 1, entry 9) gave **11** in an excellent 84% yield. A small of amount of reagent degradation could account for the need for a slight excess of the peroxide reagent.

Following the development of an optimized set of conditions, we aimed to gain a mechanistic understanding of the transformation. Two potential pathways are outlined in Scheme 4. An initial interaction between the peroxide **7** and alkene **12** forms the first C−O bond and a stabilized benzylic carbocation **13**. Direct cyclization of **13** results in the formation of dioxonium intermediate **14**. Hydrolysis of **14**, followed by decarboxylation, provides the observed products **16** and **17**. An alternative pathway that is also consistent with the products involves direct decarboxylation and cyclization to give the 2-cyclobutylidene-1,3-dioxolane **18**. Subsequent protonation and hydrolytic decomposition then leads to **16** and **17**. If the second alternative is operating, **18** would be highly reactive, and it is not clear why it selectively protonates in preference to reacting with a second molecule of peroxide **7**. Further investigation is required to deconvolute the subtleties in the mechanistic pathway.

Both of these preliminary mechanisms are supported by isotopic labeling studies (Scheme 5). The use of $^{18}OH_2$ results in exclusive incorporation of the ^{18}O label within the carbonyl group (**22** and **23**), consistent with Scheme 4 and previous observations that water was vital to reaction success. Use of deuterium oxide as the water source resulted in >80%

Scheme 3. Reaction of Cyclobutane Malonoyl Peroxide 1 with 4-Methylstyrene 8



8 **9** **10** **11**

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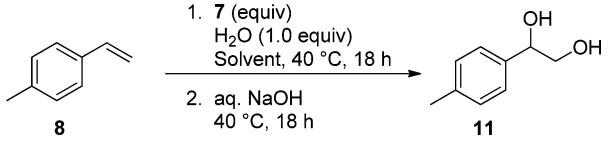
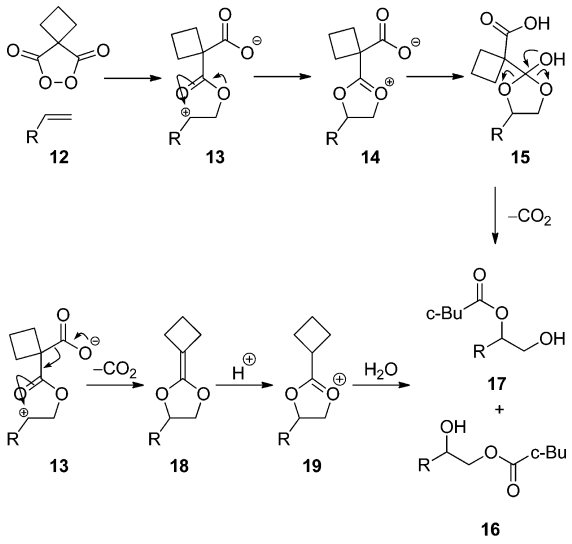
Table 1. Optimization of Reaction Conditions for Dihydroxylation of 4-Methyl Styrene 8[a]



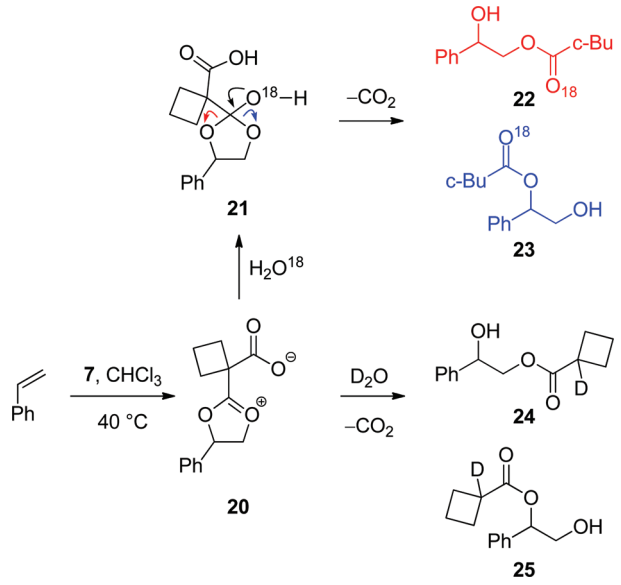
entry	solvent	H_2O equiv	peroxide equiv	yield[b] (%)
1	CH_3CN (bench)		1.5	20–55
2	CH_3CN (dry)	0	1.5	20
3	CH_3CN	1.0	1.5	55
4	$CHCl_3$	1.0	1.5	69
5	THF	1.0	1.5	30
6	PhMe	1.0	1.5	60
7	MeOH	1.0	1.5	0
8	$CHCl_3$	1.0	1.0	78
9	$CHCl_3$	1.0	1.1	84
10	$CHCl_3$	1.0	2.0	44
11	$CHCl_3$	1.0	3.0	22

[a]Reactions performed at 0.8 M on a 1 mmol scale of alkene. [b]Isolated yield after column chromatography.

Scheme 4. Potential Mechanisms for the Cyclobutane Malonoyl Peroxide 7 Mediated Dihydroxylation



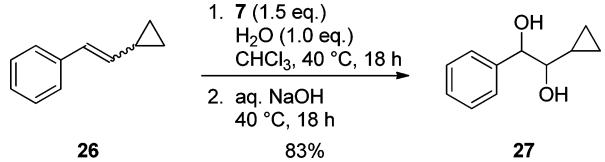
Scheme 5. Labeling Studies for Reaction between Styrene and 7



deuterium incorporation in the products **24** and **25** as confirmed by ^1H, ^{13}C and, ^2D NMR spectroscopy.

It is possible that a radical, single electron transfer (SET), or ionic mechanism is operating during the reaction of the alkene and the peroxide. The addition of 0.1 equiv of butylated hydroxy toluene (BHT), a well-known radical inhibitor, resulted in minimal change to reaction rate and isolated yield of **22** and **23**. These results suggested that a radical mechanism was not operating. Reports by Schuster[28,29] have shown malonoyl peroxides to undergo reaction with polyconjugated aromatics via SET. The possibility exists for the initial C–O bond-forming event between **7** and the alkene to proceed via SET. Cyclopropyl carbinyl radicals are known to undergo rapid ring-opening to give butenyl radicals.[30] To probe this phenomenon further, 1-phenyl-2-cyclopropylethylene **26** was examined as a substrate in the reaction with **7** (Scheme 6). Under standard reaction conditions ($CHCl_3$, 1 equiv of H_2O, 40 °C, 18 h), the diol **27** was isolated in 83% yield after hydrolysis. This result does not provide conclusive evidence

Scheme 6. Reaction of 1-Phenyl-2-cyclopropylethylene with 7



against a SET mechanism operating, and further investigation is required to establish in favor of an ionic or SET pathway.

The substrate scope was examined with a series of commercially available styrene derivatives (Table 2). It should be noted that a number of alkene substrates were not consumed using 1.1 equiv of **7**. The use of 1.5 equiv of **7** consistently led to consumption of the alkene starting material and was used as standard without significantly affecting the isolated yields. The effect of varying substitution pattern was examined with 3- and 2-methyl styrene (Table 2, entries 2 and

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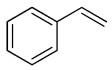
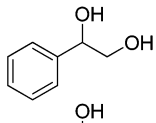
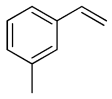
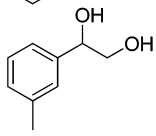
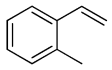
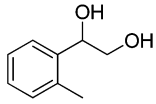
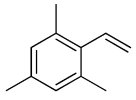
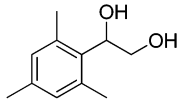
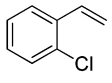
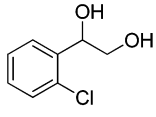
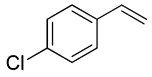
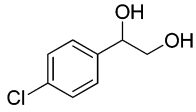
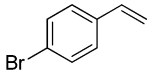
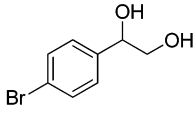
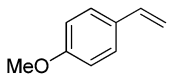
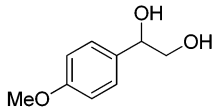
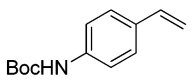
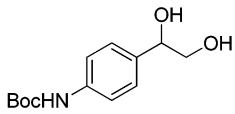
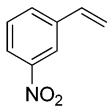
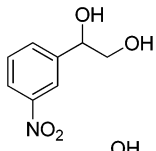
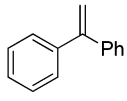
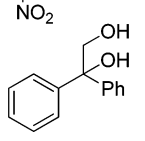
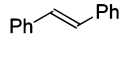
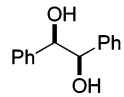
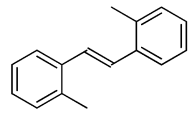
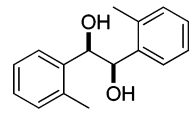
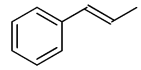
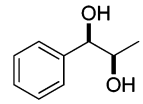
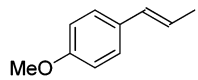
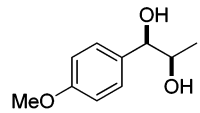
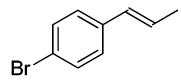
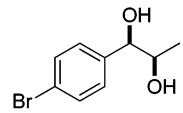
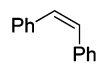
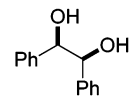
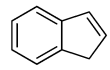
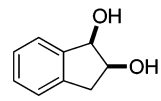
Table 2. Substrate Scope for the Cyclobutane Malonoyl Peroxide (7) Mediated Dihydroxylation[a]

entry	substrate	product	yield (%)[b]
1			78
2			65
3			80
4			65
5			38
6			77
7			74
8			78
9			56
10[c]			30
11			67

[a]Standard conditions: (i) alkene (1 mmol), 7 (1.5 mmol), H_2O (1 equiv), $CHCl_3$ (1.4 mL), 40 °C, 18−24 h; (ii) reduce to dryness, then 1 M NaOH (10 mL), 40 °C, 18 h. [b]Isolated yield. [c]2.0 mmol 7 used for 68 h.

3), which were dihydroxylated in 65 and 80% isolated yield, respectively. Pleasingly, the sterically demanding mesityl group was also tolerated (Table 2, entry 4), providing the diol in 65%. The effect of substitution pattern was further probed with 2-chlorostyrene, which gave the dihydroxylated product in significantly lower yield (Table 2, entry 5; 38%). The reaction was also found to be unaffected by the presence of halogens (Table 2, entries 6 and 7). Cyclobutane malonoyl peroxide **7** is an electrophilic reagent, and as a result, dihydroxylation of electron-deficient alkenes represents a considerable challenge. In contrast, electron-rich alkenes represent the most likely substrates to give higher reaction rate. The reaction between cyclobutane malonoyl peroxide **7** and 3-nitrostyrene was slow and required the use of excess peroxide (2.0 equiv) and extended reaction times (68 h) to give the corresponding diol in a disappointingly low yield of 30% (Table 2, entry 10). Attention is drawn to the fact that unreacted starting material could be observed in the ^1H NMR of the crude reaction mixture, indicating that further optimization on this substrate is possible. As predicted, 4-methoxystyrene was dihydroxylated in good yield (78%), although no appreciable increase in rate was noted (Table 2, entry 8). 1,1-Disubstituted alkenes were also tolerated as exemplified by the dihydroxylation of 1,1-diphenylethylene in 67% (Table 2, entry 11).

Table 3. Stereoselectivity for the Cyclobutane Malonoyl Peroxide Mediated Dihydroxylation[a]

entry	substrate	product	yield(%)[b] (*syn*:*anti*)[c]
1			78 (28:1)
2			78 (32:1)
3			80 (4:1)
4			77 (6:1)
5			70 (6:1)
6			78 (3:1)
7			67 (>50:1)

[a]Standard conditions: (i) alkene (1 mmol), 7 (1.5 mmol), H_2O (1 equiv), $CHCl_3$ (1.4 mL), 40 °C, 18−24 h; (ii) reduce to dryness, then 1 M NaOH (10 mL), 60 °C, 4 h. [b]Isolated yield. [c]Determined by ^1H NMR spectroscopy of crude reaction mixture.

1,2-Disubstituted alkenes presented an opportunity to evaluate the stereoselectivity associated with the transformation (Table 3). The dihydroxylation of *trans*-stilbene gave a mixture of (±)- and *meso*-hydrobenzoin (78%; 28:1), indicating that the reaction is not stereospecific. The loss of stereochemical integrity can be attributed to the formation of a benzylic carbocation (c.f. **13**, Scheme 4), at which point free rotation about the C−C bond is possible, allowing the formation of both diastereoisomers. Excellent *syn*-selectivity is observed with

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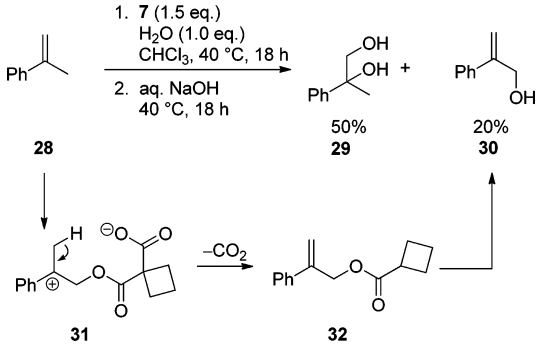
trans-stilbene derivatives with *syn*:*anti* ratios >28:1 being achieved (Table 3, entries 1 and 2). Dihydroxylation of *β*-methylstyrene derivatives led to a decrease in the diastereoselectivity with *syn*:*anti* ratios ∼5:1 being achieved (Table 3, entries 3−5). It is interesting to note that substituents that stabilize (Table 3, entry 4) or destabilize (Table 3, entry 5) a benzylic carbocation had little effect on the observed diastereoselectivities as illustrated by 4-methoxy- and 4-bromo-*β*-methylstyrene. *cis*-Stilbene was found to give the dihydroxylated product with a lower diastereoselectivity (Table 3, entry 6; *syn*:*anti* 3:1); however, incorporation of a *cis*-alkene within a ring resulted in the exclusive formation of the *syn*-dihydroxylated product (Table 3, entry 7; 67%).

Although the majority of the substrates tested gave the dihydroxylated product exclusively, a number of unexpected side products were observed throughout reaction development. Alkenes containing *β*-hydrogens, such as *α*-methylstyrene **28**, gave a mixture of dihydroxylated product **29** (50%) and allylic alcohol **30** (20%) (Scheme 7).

Scheme 7. Allylic Alcohol Formation with Alkenes Bearing B-Hydrogens

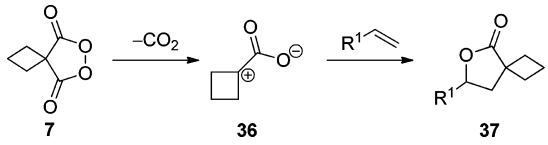


Formation of **30** was attributed to loss of an allylic hydrogen following the formation of the benzylic carbocation **31**. Subsequent decarboxylation gave the stable allylic ester **32**, which was hydrolyzed without purification to give **30** as a product. The direct conversion of an alkene to an allylic alcohol represents a useful transformation,[31] and we are currently investigating the potential of forming the allylic alcohol exclusively.

An additional set of unusual products were observed following the attempted dihydroxylation of 4-hydroxystyrene (Table 4, entry 1). Curiously, the reaction resulted in the formation of a *γ*-lactone in low yield (Table 4, entry 1). Further investigation revealed *γ*-lactone formation was also observed for 2-hydroxystyrene and 4-*N*-Boc-aminostyrene (Table 4, entries 2 and 3).

A potential explanation for the formation of lactones **33**−**35** involves the formation of zwitterion **36** following loss of CO_2 from **7**. Subsequent addition of **36** across the alkene substrate generates the observed products. Formation of zwitterion **36** has been previously proposed by Adam and co-workers during their investigation into the formation of *α*-lactones from malonoyl peroxides.[32] Although providing a plausible mechanism for *γ*-lactone formation, it is currently unclear how the alkene substrate brings about such a dramatic change in reactivity and highlights mechanistic subtleties that are still to be fully understood (Scheme 8).

Scheme 8. Potential Mechanism for γ-Lactone Formation

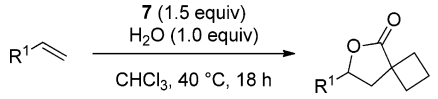


Comparison of cyclopropane malonoyl peroxide **38** and cyclobutane malonoyl peroxide **7** reveals a series of noteworthy similarities and differences. Synthesis of each reagent proceeds in the same yield, and they both lead to the *syn*-dihydroxylated product with similar levels of selectivity. As reported previously,[23] reactions of cyclopropyl malonoyl peroxide proceed at a faster rate, but it is important to note that the ability to slow down the reaction could have significant implications in the development of a catalytic procedure. The major difference between the two reagents resides in the reaction mechanism. Reaction of **7** with 4-methylstyrene leads to the intermediates **9** and **10**, where decarboxylation has taken place. Reaction of **38** with 4-methylstyrene leads to the intermediates **39** and **40**, where the carboxylic acid group is still present (Scheme 9). It is possible that this observation provides evidence for intermediate **18** (Scheme 4). When using cyclopropane malonoyl peroxide **38**, formation of the analogous intermediate **41** would be disfavored because of the formation of an sp^2 hybridized center on the cyclopropane ring. The ability of **7** to decarboxylate allows for different reactivity, for example, formation of the *γ*-lactones **33**−**35**. These products suggest that cyclobutane malonoyl peroxide may possess unexpected forms of reactivity that are yet to be fully exploited. Further investigations in this area may reveal additional synthetically interesting transformations.

CONCLUSION

In summary, we have described an operationally simple method for the dihydroxylation of alkenes using cyclobutane malonoyl peroxide **7**. The reagent is easily prepared from the commercially available diacid and can be used to dihydroxylate

Table 4. γ-Lactone Formation[a]



entry	R^1	product	yield[b] (%)
1	4-OH-C_6H_4	**33**	19
2	2-OH-C_6H_4	**34**	45
3	4-NHBoc-C_6H_4	**35**	30

[a]Reactions performed at 0.8 M on a 1 mmol scale. [b]Isolated yield after column chromatography.

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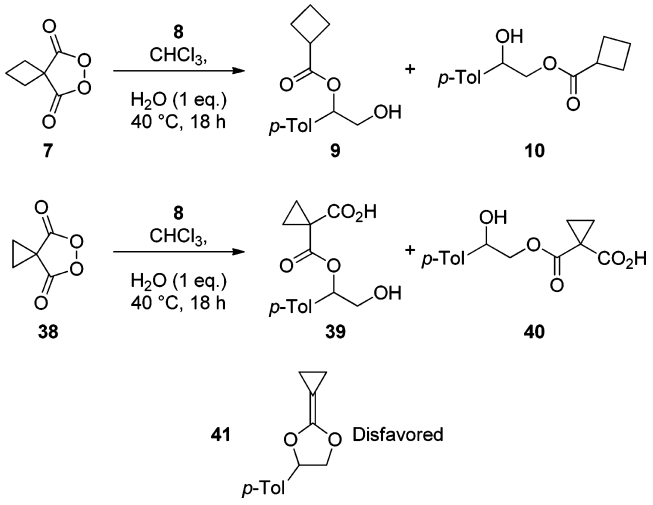
Scheme 9. Comparison of Reactivity of Cyclobutane Malonoyl Peroxide 7 and Cyclopropane Malonoyl Peroxide 38



a range of styrene and stilbene derivatives in good yield, often without column chromatography. Competitive diastereoselectivities have been achieved for a range of 1,2-disubstituted alkenes. A plausible mechanism has been proposed, which is supported by isotopic labeling studies; however, the formation of side products has been included to illustrate that there are still mechanistic questions that require further understanding. Along with developing a more accurate description of the reaction mechanism, current work is focused on the development of a catalytic variant of the reaction.

EXPERIMENTAL SECTION

Caution: Peroxides are particularly dangerous. These procedures should be carried out only by knowledgeable laboratory workers.

Cyclobutane Malonoyl Peroxide 7.[32] Methane sulfonic acid (30 mL) was placed in a round bottomed flask equipped with large magnetic stirrer bar and immersed in a bath of water at 22 °C. Urea hydrogen peroxide (9.8 g, 104 mmol) was added in a single portion, and the mixture was stirred for 30 s. Cyclobutane-1,1-dicarboxylic acid (5.0 g, 35 mmol) was added in a single portion, and the reaction was stirred vigorously for 18 h. The reaction mixture was poured into a mixture of ice (80 g) and ethyl acetate (100 mL), and the layers were separated. The aqueous layer was washed with ethyl acetate (2 × 100 mL), and the combined organic layers were washed with $NaHCO_3$ (2 × 50 mL) and brine (20 mL) and dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the title compound 7 as a white solid (4.0 g, 80%): mp 63 °C; IR (thin film)/cm^{-1} 1799, 1269; ^1H NMR (250 MHz, $CDCl_3$) δ 2.71 (t, J = 8.0 Hz, 4H), 2.36 (quin, J = 8.0 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 173.9, 40.4, 28.9, 16.3.

General Procedure for the Dihydroxylation of Alkenes with Cyclobutane Malonoyl Peroxide. 1-*p*-Tolylethane-1,2-diol 11.[33] Alkene (0.7 mmol) was added dropwise to a solution of cyclobutane malonoyl peroxide (0.15 g, 1.1 mmol) in chloroform (1.4 mL). H_2O (13 μL, 0.7 mmol) was added, and the reaction mixture was heated at 40 °C for 18−24 h. The resulting solution was reduced to dryness, and 1 M NaOH (10 mL) was added. The reaction mixture was heated at 40 °C for 18 h. The aqueous layer was extracted with chloroform (15 mL). The aqueous layer was further extracted with chloroform (2 × 20 mL), and the combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure to give the desired diol: mp 70−72 °C; IR (thin film)/cm^{-1} 3371, 2925, 1647, 1327; ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 4.74 (dd, J = 3.5, 8.4 Hz, 1H), 3.67 (dd, J = 3.5, 11.5 Hz, 1H), 3.60 (dd, J = 8.4, 11.5 Hz, 1H), 3.48 (s, 1H), 3.19 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 137.5, 137.4, 129.1, 126.0, 74.5, 68.0, 21.1; LRMS (EI) m/z 152.1 $[M]^+$; HRMS (EI) calculated for $C_9H_{12}O_2$ $[M]^+$ 152.0837, found 152.0840.

1-(*O*-Oxocyclobutyl)-1-(*p*-tolyl) Ethane-1,2-diol 9. Colorless oil (0.12 g, 45%): IR (thin film)/cm^{-1} 3480, 3018, 1728, 1252; ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 5.73 (dd, J = 4.1, 7.7 Hz, 1H), 3.78 (dd, J = 7.7, 12.0 Hz, 1H), 3.70 (dd, J = 4.1, 12.0 Hz, 1H), 3.14 (quin, J = 8.5 Hz, 1H), 2.25 (s, 3H), 2.24−2.11 (m, 4H), 1.91−1.82 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 175.1, 138.2, 134.3, 129.3, 126.5, 76.5, 66.1, 38.2, 25.3, 25.1, 21.2, 18.4; LRMS (EI) m/z 216.1 $[M - H_2O]^+$; HRMS (EI) calculated for $C_{14}H_{16}O_2$ $[M - H_2O]^+$ 216.1150, found 216.1148.

2-(*O*-Oxocyclobutyl)-1-(*p*-tolyl) Ethane-1,2-diol 10. Colorless oil (0.10 g, 37%): IR (thin film)/cm^{-1} 3471, 3066, 1726, 1252, 1215; ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 4.84 (dd, J = 3.2, 8.3 Hz, 1H), 4.19 (dd, J = 3.3, 11.6 Hz, 1H), 4.08 (dd, J = 8.4, 11.6 Hz, 1H), 3.11 (quin, J = 8.5 Hz, 1H), 2.50 (bs, 1H), 2.27 (s, 3H), 2.24−2.11 (m, 4H), 1.91−1.83 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 175.7, 137.9, 137.0, 129.2, 126.1, 72.4, 69.2, 38.0, 25.3, 21.1, 18.4; LRMS (EI) m/z 216.1 $[M - H_2O]^+$; HRMS (EI) calculated for $C_{14}H_{16}O_2$ $[M - H_2O]^+$ 216.1150, found 216.1150.

2-Phenylpropane-1,2-diol 29.[34] Colorless oil (0.05 g, 50%): IR (thin film)/cm^{-1} 3568, 1449, 1027; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.32 (m, 2H), 7.27−7.24 (m, 2H), 7.19−7.15 (m, 1H), 3.62 (d, J = 11.2 Hz, 1H), 3.48 (d, J = 11.2 Hz, 1H), 2.90 (s, 2H), 1.39 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 144.9, 128.3, 127.0, 125.0, 74.8, 70.8, 25.9; LRMS (EI) m/z 134.1 $[M - H_2O]^+$; HRMS (EI) calculated for $C_9H_{10}O$ $[M - H_2O]^+$ 134.0732, found 134.0736.

2-Phenylprop-2-en-1-ol 30.[35] Colorless oil (0.02 g, 20%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.47−7.44 (m, 2H), 7.38−7.31 (m, 3H), 5.48 (app s, 1H), 5.36 (s, 1H), 4.56 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 138.5, 128.5, 127.9, 126.1, 112.6, 65.1; LRMS (EI) m/z 134.1 $[M]^+$; HRMS (EI) calculated for $C_9H_{10}O$ $[M]^+$ 134.0732, found 134.0729.

1-Phenylethane-1,2-diol. Table 2, entry 1: mp 61 °C; IR (thin film)/cm^{-1} 3394, 2926, 1613; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37−7.29 (m, 5H), 4.83 (dd, J = 3.6, 8.4 Hz, 1H), 3.76 (dd, J = 3.6, 11.6 Hz, 1H), 3.66 (dd, J = 8.4, 11.2 Hz, 1H), 2.67 (s, 1H), 2.26 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 128.5, 128.0, 126.0, 74.7, 68.1; LRMS (EI) m/z 138.1 $[M]^+$; HRMS (EI) calculated for $C_8H_{10}O_2$ $[M]^+$ 138.0681, found 138.0676.

1-*m*-Tolylethane-1,2-diol. Table 2, entry 2: mp 70−72 °C; IR (thin film)/cm^{-1} 3159, 2924, 1483; ^1H NMR (400 MHz, $CDCl_3$) δ 7.15−7.12 (m, 1H), 7.04−7.00 (m, 3H), 4.65 (dd, J = 3.6, 8.4 Hz, 1H), 3.59 (dd, J = 3.2, 11.6 Hz, 1H), 3.51 (dd, J = 8.4, 11.6 Hz, 1H), 3.44 (bs, 2H), 2.24 (s, 3H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 140.4, 138.1, 128.6, 128.3, 126.7, 123.1, 74.7, 68.0, 21.4; LRMS (EI) m/z 152.1 $[M]^+$; HRMS (EI) calculated for $C_9H_{12}O_2$ $[M]^+$ 152.0837, found 152.0836.

1-*o*-Tolylethane-1,2-diol.[36] Table 2, entry 3: mp 104−105 °C; IR (thin film)/cm^{-1} 3258, 2924, 1356, 1066; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, J = 1.6, 7.6 Hz, 1H), 7.24−7.14 (m, 3H), 5.06 (dd, J = 3.2, 8.4 Hz, 1H), 3.73 (dd, J = 3.2, 11.6 Hz, 1H), 3.61 (dd, J = 8.4, 11.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.4, 134.7, 130.4, 127.7, 126.3, 125.6, 71.4, 66.9, 19.0; LRMS (EI) m/z 152.1 $[M]^+$; HRMS (EI) calculated for $C_9H_{12}O_2$ $[M]^+$ 152.0837, found 152.0842.

1-Mesitylethane-1,2-diol.[37] Table 2, entry 4: mp 110−111 °C; IR (thin film)/cm^{-1} 3365, 2923, 1611; ^1H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 5.26 (dd, J = 3.6, 10.0 Hz, 1H), 3.96 (dd, J = 10.0, 11.6 Hz, 1H), 3.61 (dd, J = 3.8, 11.6 Hz, 1H), 2.40 (s, 6H), 2.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.2, 136.6, 132.4, 130.2, 72.6, 64.6, 20.7, 20.7; LRMS (EI) m/z 180.1 $[M]^+$; HRMS (EI) calculated for $C_{11}H_{16}O_2$ $[M]^+$ 180.1150, found 180.1145.

1-(2-Chlorophenyl)ethane-1,2-diol. Table 2, entry 5: mp 101−104 °C; IR (thin film)/cm^{-1} 3164, 1470, 1361, 1068; ^1H NMR (250 MHz, $CDCl_3$) δ 7.60 (dd, J = 1.9, 7.4 Hz, 1H), 7.35−7.22 (m, 3H), 5.25 (dd, J = 3.0, 8.0 Hz, 1H), 3.91 (dd, J = 2.8, 11.3 Hz, 1H), 3.58

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(dd, J = 8.0, 11.3 Hz, 1H), 2.73 (bs, 1H), 2.18 (bs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.8, 132.0, 129.4, 129.0, 127.6, 127.1, 71.4, 66.2; LRMS (EI) m/z 172.0 $[M]^+$; HRMS (EI) calcd for $C_8H_9O_2Cl^{35}$ $[M]^+$ 172.0291, found 172.0288.

1-(4-Chlorophenyl)ethane-1,2-diol. Table 2, entry 6: mp 76−77 °C; IR (thin film)/cm^{-1} 3612, 3399, 1598, 1077; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.29 (m, 4H), 4.80 (dd, J = 3.6, 8.4 Hz, 1H), 3.74 (dd, J = 3.6, 11.2 Hz, 1H), 3.61 (dd, J = 8.0, 11.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 133.8, 128.7, 127.4, 74.0, 67.9; LRMS (CI) m/z 190.2 $[M + NH_4]^+$; HRMS (ES) calcd for $C_8H_{13}O_2Cl^{35}N$ $[M + NH_4]^+$ 190.0629, found 190.0626.

1-(4-Bromophenyl)ethane-1,2-diol. Table 2, entry 7: mp 98−99 °C; IR (thin film)/cm^{-1} 3313, 2930, 1590; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 4.73−4.69 (m, 1H), 4.43 (d, J = 3.6 Hz, 1H), 3.87 (t, J = 6.0 Hz, 1H), 3.65−3.50 (m, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 139.4, 131.6, 127.8, 121.8, 74.0, 67.9; LRMS (EI) m/z 216.0 $[M]^+$; HRMS (EI) calcd for $C_8H_9O_2Br^{79}$ $[M]^+$ 215.9786, found 215.9790.

1-(4-Methoxyphenyl)ethane-1,2-diol. Table 2, entry 8: mp 78−79 °C; IR (thin film)/cm^{-1} 3359, 2935, 2839, 1612, 1246; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.78 (dd, J = 3.4, 7.8 Hz, 1H), 3.81 (s, 3H), 3.76−3.63 (m, 2H), 2.42 (bs, 1H), 2.03 (bs, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 159.3, 132.6, 127.3, 113.9, 74.3, 68.0, 55.3; LRMS (EI) m/z 168.2 $[M]^+$; HRMS (ES) calcd for $C_9H_{12}O_3Na$ $[M + Na]^+$ 191.0679, found 191.0676.

***tert*-Butyl 4-(1,2-Dihydroxyethyl)phenylcarbamate.** Table 2, entry 9: mp 139−141 °C; IR (thin film)/cm^{-1} 3379, 3334, 3281, 2933, 1685, 1525; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.43 (bs, 1H), 4.71 (dd, J = 3.6, 8.0 Hz, 1H), 3.66 (dd, J = 3.6, 11.2 Hz, 1H), 3.57 (dd, J = 8.4, 11.2 Hz, 1H) 1.45 (s, 9H); ^{13}C NMR (125 MHz, DMSO) δ 152.7, 138.0, 136.9, 126.3, 117.6, 78.7, 73.3, 67.4, 28.0; LRMS (EI) m/z 253.1 $[M]^+$; HRMS (EI) calcd for $C_{13}H_{19}NO_4$ $[M]^+$ 253.1314, found 253.1310.

1-(3-Nitrophenyl)ethane-1,2-diol.[38] Table 2, entry 10: mp 74−75 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.30 (d, J = 1.6 Hz, 1H), 8.13−8.11 (m, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.62 (t, J = 8.0 Hz, 1H), 4.89 (dd, J = 3.4, 7.9 Hz, 1H), 4.79 (d, J = 4.0 Hz, 1H), 4.08 (t, J = 5.6 Hz, 1H), 3.75−3.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 132.2, 129.5, 122.9, 121.2, 73.5, 67.7 (one carbon missing); LRMS (EI) m/z 165.0 $[M - H_2O]^+$; HRMS (EI) calcd for $C_8H_7O_3N$ $[M - H_2O]^+$ 165.0426, found 165.0434.

1,1-Diphenylethane-1,2-diol. Table 2, entry 11: mp 110 °C; IR (thin film)/cm^{-1} 3372, 3303, 1491, 1455, 1384, 1361, 1043; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.36 (m, 4H), 7.29−7.26 (m, 4H), 7.22−7.18 (m, 2H), 4.10 (d, J = 6.4 Hz, 2H), 3.11 (s, 1H), 1.80 (t, J = 6.4 Hz, 1H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 143.7, 128.4, 127.5, 126.4, 78.5, 69.4; LRMS (EI) m/z 196.1 $[M - H_2O]^+$; HRMS (EI) calcd for $C_{14}H_{12}O$ $[M - H_2O]^+$ 196.0888, found 196.0887.

(±)-Hydrobenzoin. Table 3, entry 1: mp 104−105 °C; IR (thin film)/cm^{-1} 3389, 2922, 2852, 1645; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−7.06 (m, 10H), 4.66 (s, 2H), 2.74 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 128.1, 127.9, 126.9, 79.1; LRMS (APCI) m/z 196.1 $[M - H_2O]^+$; HRMS (CI) calcd for $C_{14}H_{14}O_2Na$ $[M + Na]^+$ 237.0886, found 237.0887.

***rel*-(1*R*,2*R*)-1,2-Di-*o*-tolylethane-1,2-diol.** Table 3, entry 2: mp 125 °C; IR (thin film)/cm^{-1} 3390, 1604, 1490; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 1.2, 7.6 Hz, 2H), 7.22−7.18 (m, 2H), 7.14−7.10 (m, 2H), 6.92 (d, J = 7.6 Hz, 2H), 4.93 (s, 2H), 3.22 (s, 2H), 1.64 (s, 6H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 137.9, 135.8, 130.0, 127.6, 127.1, 125.8, 74.5, 18.7; LRMS (EI) m/z 224.1 $[M - H_2O]^+$; HRMS (EI) calcd for $C_{16}H_{16}O$ $[M - H_2O]^+$ 224.1201, found 224.1203.

***rel*-(1*R*,2*R*)-1-Phenylpropane-1,2-diol.**[39] Table 3, entry 3: IR (thin film)/cm^{-1} 3435, 1714, 1520, 1392; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.31 (m, 5H), 4.38 (d, J = 7.6 Hz, 1H), 3.90−3.84 (m, 1H), 2.32 (bs, 2H), 1.07 (d, J = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0, 128.4, 128.0, 126.8, 79.4, 72.2, 18.7; LRMS (EI) m/z 134.1 $[M - H_2O]^+$; HRMS (EI) calcd for $C_9H_{10}O$ $[M - H_2O]^+$ 134.0732, found 134.0730.

***rel*-(1*R*,2*R*)-1-(4-Methoxyphenyl)propane-1,2-diol.**[40] Table 3, entry 4: IR (thin film)/cm^{-1} 3390, 2979, 2901, 1485, 1397; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.4 Hz, 2H), 4.17 (d, J = 8.0 Hz, 1H), 3.70 (s, 3H), 3.75−3.65 (m, 1H), 0.89 (d, J = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 133.2, 128.0, 113.9, 79.1, 72.2, 55.2, 18.7; LRMS (EI) m/z 182.1 $[M]^+$; HRMS (EI) calcd for $C_{10}H_{14}O_3$ $[M]^+$ 182.0943, found 182.0940.

***rel*-(1*R*,2*R*)-1-(4-Methoxyphenyl)propane-1,2-diol.**[41] Table 3, entry 5: IR (thin film)/cm^{-1} 3402, 2896, 1593, 1488, 1400, 1126, 1069, 1040, 1010, 926; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 4.30 (d, J = 7.2 Hz, 1H), 3.80−3.74 (m, 1H), 2.72 (bs, 2H), 1.03 (d, J = 6.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 131.6, 128.5, 122.0, 78.8, 72.1, 18.8; LRMS (EI) m/z 211.9 $[M - H_2O]^+$; HRMS (EI) calcd for $C_9H_9OBr^{79}$ $[M - H_2O]^+$ 211.9837, found 211.9841.

***meso*-Hydrobenzoin.** Table 3, entry 6: mp 133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.17 (m, 10H), 4.76 (s, 2H), 2.13 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 128.2, 128.1, 127.1, 78.1; LRMS (EI) m/z 196.1 $[M - H_2O]^+$; HRMS (EI) calcd for $C_{14}H_{12}O$ $[M - H_2O]^+$ 196.0888, found 196.0886.

***rel*-(1*R*,2*S*)-2,3-Dihydro-1*H*-indene-1,2-diol.** Table 3, entry 7: mp 88−90 °C; IR (thin film)/cm^{-1} 3395, 2924, 1727, 1610; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.36−7.33 (m, 1H), 7.20−7.18 (m, 3H), 4.88 (d, J = 4.8 Hz, 1H), 4.40−4.35 (m, 1H), 3.03 (dd, J = 5.8, 16.3 Hz, 1H), 2.85 (dd, J = 3.6, 16.3 Hz, 1H), 2.50 (bs, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 141.9, 140.1, 128.8, 127.2, 125.3, 125.0, 75.9, 73.4, 38.6; LRMS (EI) m/z 150.1 $[M]^+$; HRMS (EI) calcd for $C_9H_{10}O_2$ $[M]^+$ 150.0681, found 150.0684.

General Procedure for the Formation of γ-Lactones. Alkene (0.7 mmol) was added to a solution of cyclobutane malonoyl peroxide (0.15 g, 1.0 mmol) in chloroform (2 mL). After ∼5 min, the reaction mixture turned orange. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was reduced to dryness to give the corresponding γ-lactone, which was purified by column chromatography.

5-(4-Hydroxyphenyl)-3,3-spirocyclobutylbutyrolactone 33. Spectral data: mp 140−141 °C; IR (thin film)/cm^{-1} 3369, 2940, 1753, 1614, 1517, 1447, 1330, 1172; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 8.3 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 5.66 (bs, 1H), 5.29 (dd, J = 6.0, 9.3 Hz, 1H), 2.72 (dd, J = 6.0, 13.0 Hz, 1H), 2.62−2.46 (m, 2H), 2.26 (dd, J = 9.0, 13.0 Hz, 1H), 2.19−1.94 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.1, 155.9, 131.0, 127.2, 115.6, 78.2, 44.9, 44.4, 31.6, 29.1, 16.5; LRMS (EI) m/z 218.1 $[M]^+$; HRMS (MALDI) calcd for $C_{13}H_{14}O_3$ $[M]^+$ 218.0943, found 218.0937.

5-(2-Hydroxyphenyl)-3,3-spirocyclobutylbutyrolactone 34. Spectral data: mp 169−171 °C; IR (thin film)/cm^{-1} 3365, 2944, 1749, 1603, 1457, 1333; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.16 (m, 2H), 6.93−6.83 (m, 2H), 6.20 (bs, 1H), 5.64 (dd, J = 6.8, 8.4 Hz, 1H), 2.86 (dd, J = 6.8, 13.0 Hz, 1H), 2.60−2.50 (m, 2H), 2.33 (dd, J = 8.4, 13.0 Hz, 1H), 2.20−1.97 (m, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 181.7, 153.0, 129.2, 125.9, 125.6, 120.6, 115.8, 75.3, 44.5, 42.7, 31.6, 29.5, 16.5; LRMS (EI) m/z 218.1 $[M]^+$; HRMS (EI) calcd for $C_{13}H_{14}O_3$ $[M]^+$ 218.0943, found 218.0943.

5-(4-*N*-Boc-Phenyl)-3,3-spirocyclobutylbutyrolactone 35. Spectral data: mp 115 °C; IR (thin film)/cm^{-1} 3437, 1764, 1725, 1597, 1524; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 8.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 6.61 (bs, 1H), 5.29 (dd, J = 6.5, 9.0 Hz, 1H), 2.72 (dd, J = 6.5, 13.0 Hz, 1H), 2.60−2.47 (m, 2H), 2.22 (dd, J = 9.0, 13.0 Hz, 1H), 2.17−1.92 (m, 4H), 1.50 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 180.7, 152.7, 138.6, 133.7, 126.3, 118.6, 80.7, 77.8, 44.8, 44.5, 31.5, 29.2, 28.3, 16.5; LRMS (EI) m/z 317.2 $[M]^+$; HRMS (EI) calcd for $C_{18}H_{23}O_4N$ $[M]^+$ 317.1627, found 317.1631.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C spectra for all compounds reported. This material is available free of charge via the Internet at http://pubs.acs.org.

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