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Triflic Acid Catalyzed Oxidative Lactonization and Diacetoxylation of Alkenes Using Peroxyacids as Oxidants

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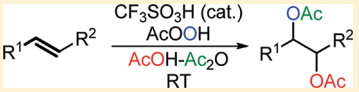
Supporting Information

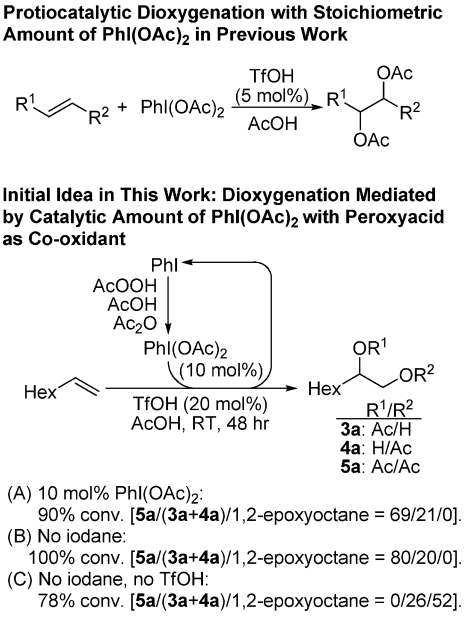
ABSTRACT: A clean and efficient diacetoxylation reaction of alkenes catalyzed by triflic acid using commercially available peroxyacids as the oxidants has been developed. This method was also applied in oxidative lactonizations of unsaturated carboxylic acids in good to high yields.



The dihydroxylation of alkenes is an important reaction in organic synthesis. Generally, there are three basic methods for the construction of 1,2-glycols: the one-step Upjohn syn-dihydroxylation[1] together with its asymmetric version developed by Sharpless,[2] the two-step reaction reported by Prévost and Woodward,[3,4] as well as the ring-opening dihydroxylation of epoxides.[5−7] The one-step processes are in principle the most efficient, but the use of highly toxic and expensive osmium tetroxide represents a serious drawback. Recently, we reported a metal free diacetoxylation of alkenes catalyzed by triflic acid using hypervalent iodine in the form of $PhI(OAc)_2$ as oxidant.[8] This reaction was previously described as metal catalyzed, involving high-valent Pd^{IV} and Cu^{III} intermediates;[9] however, a detailed mechanistic study has drawn the earlier interpretation into question.[8,9] Another recent report concerned the $Pd(OAc)_2$-catalyzed diacetoxylation of alkenes using peracetic acid as oxidant in the presence of acetic anhydride.[10] During the preparation of this manuscript, Afonso et al. described a *p*-toluenesulfonic acid (20−100 mol %) catalyzed dihydroxylation of alkenes using H_2O_2 in aqueous media at 50 °C.[11] In conclusion, the efficient dihydroxylation of alkenes with nontoxic and cheap catalysts remains a challenge.

In our previous triflic acid catalyzed diacetoxylation reaction using (diacetoxyiodo)benzene as oxidant, we found that the reaction of aliphatic alkenes normally requires elevated temperature and longer reaction times compared to arylated derivatives.[8] The use of the relatively expensive hypervalent iodine reagent, along with the production of iodobenzene as a waste, limits the scope of this synthetic method. The oxidant (diacetoxyiodo)benzene is prepared by the treatment of iodobenzene with peracetic acid in acetic acid,[12] and thus we aimed to develop a strategy using in situ generated catalytic amounts of (diacetoxyiodo)benzene in the presence of peroxyacids as co-oxidants. As shown in Scheme 1, our initial test started with the diacetoxylation of 1-octene in the presence of 10 mol % (diacetoxyiodo)benzene [$PhI(OAc)_2$] in the presence of 20 mol % triflic acid (TfOH) using 2 equiv of peracetic acid. The regeneration of hypervalent iodanes was supposed to be achieved readily with AcO_2H. In fact, the reactions with or without $PhI(OAc)_2$ gave very similar results

Scheme 1. Diacetoxylation of Alkenes Mediated by in Situ Generated Catalytic Amount of Hypervalent Iodine Reagent



(methods A and B); however, not unexpectedly, the reaction in the absence of TfOH gave 1,2-epoxyoctane as major product (method C). These findings suggested that the peroxyacid itself probably played the essential role in this reaction with TfOH acting as a catalyst or promoter.

Next, a variety of Lewis acids were investigated to identify the optimal catalytic system. As shown in Table 1, the reaction in the presence of 10 mol % of TfOH, in 20 h and at ambient temperature, gave 84% conversion, including 20% monoacetoxylation products (MAOs) and 64% 1,2-diacetoxyoctane (DAO) (entry 1). $Sn(OTf)_2$ and TMSOTf gave similar results with DAO as major product (entries 4 and 6), while the background reaction mainly furnished the epoxide (entry 5). TfOH was

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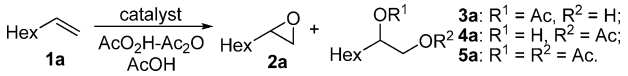
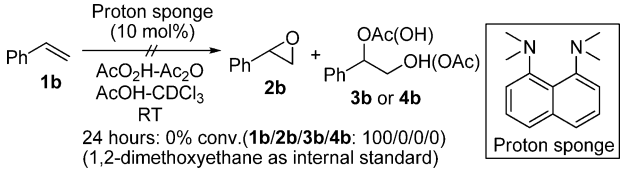
Table 1. Catalysts Screening for Peracetic Acid Dioxygenation of 1-Octene[a]



entry	catalyst	conv (%)	2a (%)	3a + 4a (%)	5a (%)
1	TfOH	84	0	20	64
2[b]	TfOH	89	0	25	64
3[c]	TfOH	100	0	82 (0)	18 (99)
4	$Sn(OTf)_2$	74	0	13	47
5[d]		78	70	4	0
6	TMSOTf	70	0	19	35
7	$Ca(OTf)_2$	70	16	38	0
8	$Ba(OTf)_2$	68	25	33	0
9	$Mg(OTf)_2$	62	3	37	0
10	$Zn(OTf)_2$	69	0	45	7
11	$AgN(Tf)_2$	67	30	19	0
12	$Cu(OTf)_2$	66	0	34	12
13[e]	$Pd(OAc)_2$	99	48	25	0
14[e,f]	$Pd(OTf)_2(L_n)$	100	0	29	12

[a]2.0 equiv of AcO_2H, 10 mol % of catalyst, room temperature (water bath), 20 h. The conversions and the ratios of the reaction mixtures were estimated on the basis of ^1H NMR using 1,2-dimethoxylethane as internal standard. [b]3-Chloroperoxybenzoic acid instead of AcO_2H. [c]Hydrogen peroxide (30%) instead of AcO_2H; the numbers in parentheses are the conversions after the treatment with Ac_2O. [d]Average of three runs for the unstable reaction. [e]Complex products, including the isomers of octenes, octadienes, and their corresponding oxidation products, Wacker−Tsuji-type oxidation products (ketones, 1- and 3-acetoxyloctenes), were seen on GC−MS. [f]$Pd(H_2O)_2(OTf)_2$(R-BINAP) was used.

Scheme 2. Inhibiting Effect of Base on the Background Epoxidation Reaction



found to have no dramatic accelerating effect in the epoxidation step but greatly enhanced the subsequent ring-opening acetoxylation of the epoxide, to the extent that no epoxide intermediate was observed under these conditions. The triflates of alkali earth metals and zinc(II) afforded moderate conversions of MAOs as major products (entries 7−10). Copper(II) triflate gave 12% of DAO and 34% MAOs (entry 12), whereas in $Pd(OAc)_2$ catalysis,[10] the conversion of 1-octene was very rapid, with only epoxide and MAOs being primarily formed (entry 13). Finally, the triflatopalladium(II) catalyst gave 12% DAO together with 29% MAOs (entry 14), along with a complex mixture of side products which were detected by GC−MS.

To further explore the catalytic and noncatalytic oxidation of 1-octene, in situ ^1H NMR studies were carried out. In Figure 1 the conversion−time plots clearly show the components of reaction mixtures. The mixture of MAOs and DAO was formed at an early stage of the TfOH catalyzed reaction (Figure 1B) while no epoxide was detected. During the course of the reaction, MAOs continuously converted to DAO, giving rise to the high final yield of DAO. The absence of epoxide in TfOH catalysis suggests extremely fast ring-opening-acetylation of the epoxide intermediate, as also found by Afonso and co-workers for the TosOH-catalyzed dihydroxylation.[11] To prove this, 1,2-epoxyoctane was subjected to a variety of reaction conditions in the presence or absence of TfOH: Whereas the epoxide disappeared prior to the first NMR experiment in the presence of TfOH (Figure 1D), only very slow conversion was observed in the back-ground reaction of ring-opening of 1,2-epoxyoctane (Figure 1C).

All reactions were run in acetic acid as reaction medium, which proved to be essential for the initial peroxyacid epoxidation step. The presence of 10 mol % of Proton Sponge totally inhibited the conversion of styrene to epoxide and its further transformations (Scheme 2).

On the basis of the aforementioned findings, an efficient metal-free diacetoxylation of alkenes catalyzed by TfOH using peroxyacids as oxidant was developed (Table 2). Under these conditions, both linear and cyclic aliphatic alkenes were converted to diacetoxylation products in good to excellent isolated yields: Terminal alkenes (entries 1−3) and cyclic alkenes (entries 6−7) gave the corresponding diacetoxylation products also in high yields. On the other hand, the extension of the carbon chain of a terminal alkene led to a decrease in yield (entry 4), as also found for aromatic alkenes such as styrenes (entries 8−9). Both *trans*- and *cis*-stilbenes gave *syn*-diacetoxylation products with low diastereoselectivities (entries 10−11). The two-step reaction using *m*-CPBA as oxidant generally afforded diacetoxylation products in higher yields (yields in parentheses in entries 1, 2, 4, and 8). Normally, the reactions using *m*-CPBA are clean, but the generation of 3-chlorobenzoic acid and its acetyl anhydride may give rise to difficulties in the purification of the reaction products on silica gel columns which is why the use of peracetic acid generally appears to be preferable.

The peroxyacid based method is also very efficient in the oxidative lactonization of ω-unsaturated carboxylic acids to afford five-membered lactones (entries 1−3, Table 3). Notably, 4-phenylpentenoic acid gave the corresponding lactone in moderate yield, whereas only a rearrangement product due to 1,2-phenyl migration was isolated in the TfOH-catalyzed lactonizations using $PhI(OAc)_2$ as the oxidant.[8] 5-Hexenoic acid and 6-heptenoic acid failed to afford the corresponding

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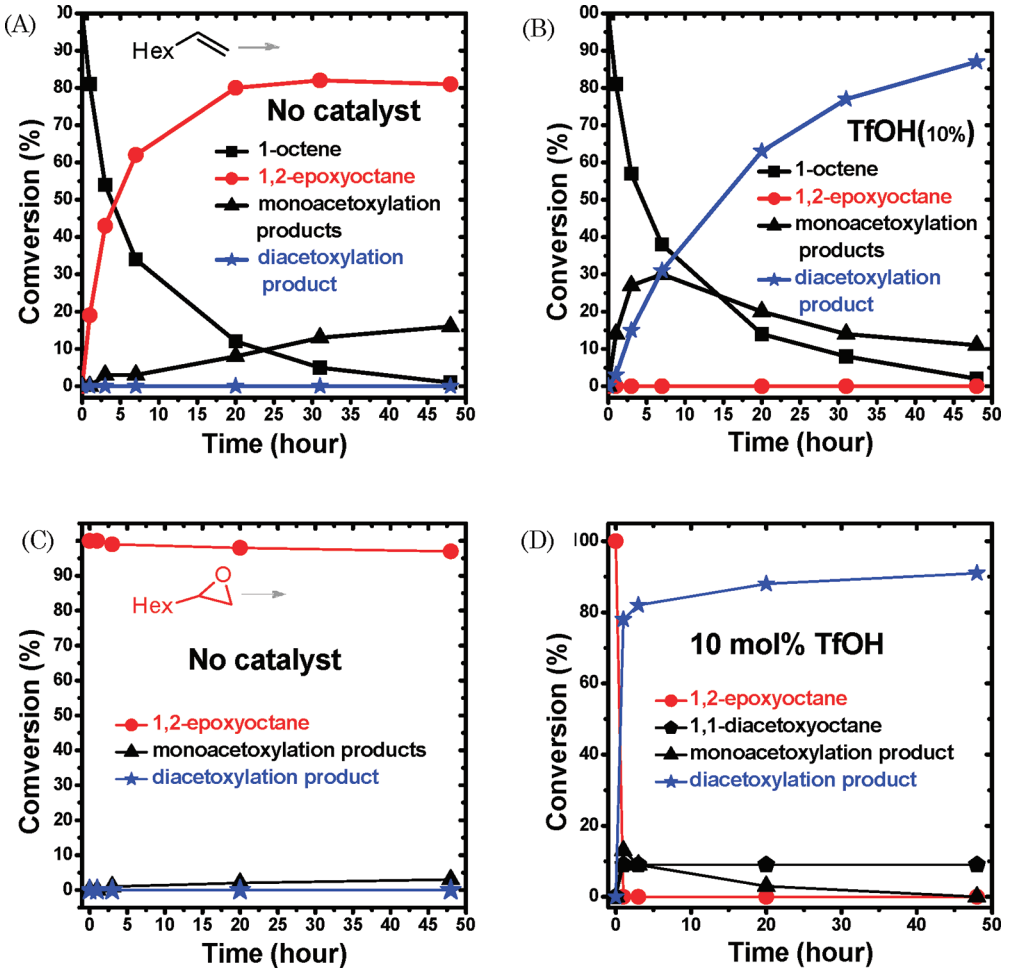

Figure 1. In situ ^{1}H NMR monitoring of the dioxygenation of 1-octene and ring opening of 1,2-epoxyoctane with peracetic acid in acetic acid in the presence of Ac_2O (1,2-dimethoxyethane as internal standard) at room temperature: (A) no catalyst; (B) 10 mol % of TfOH (No epoxide observed); (C) no catalyst; and (D) 10 mol % of TfOH (1,1-diacetoxyoctane generated via Meinwald rearrangement).

lactones but yielded the linear diacetoxylation products instead (entries 4 and 5).

A mechanism is proposed in Scheme 3. Whether catalytic or not, the dioxygenations described in this work pass through the cascade epoxidation/ring-opening of alkenes followed by acetylation. TfOH plays a dual role as catalyst for the ring-opening of the epoxide as well as following acetylation of the hydroxyl group. The reaction mechanism proposed by Afonso et al. suggests the fast formation of the epoxide catalyzed by PTSA via its corresponding peroxysulfonic acid.[11] In our case, there was no obvious catalytic effect of TfOH in epoxidation step. In the subsequent ring-opening of epoxides, both S_N2- and S_N1-type substitutions may take place, depending on the substituent R^1. If the latter stabilizes a carbocationic intermediate, ring-opening substitution mainly passes through a S_N1 pathway giving rise to the observed low diastereoselectivity.

In conclusion, we have described a metal-free, clean, and cheap diacetoxylation method for alkenes catalyzed by triflic acid using commercially available peroxyacids as oxidant. The simple and convenient operation together with its high efficiency and wide scope of alkenes render this method a viable and complementary alternative to the well-established osmium-catalyzed dihydroxylation of alkenes.

EXPERIMENTAL SECTION

Preparation of Peracetic Acid Solution (1.0 M). Peracetic acid (35.5%, 10 g, 46 mmol) was diluted with glacial acetic acid (10 mL) with the cooling of an ice−water bath, followed by the dropwise addition of 20 g of acetic anhydride under gentle shaking (CAUTION! exothermic reaction). This mixture was diluted with glacial acetic acid to a level of 1.0 M AcO_2H. The resulting solution of AcO_2H was stored at 4 °C (solidified) and warmed to room temperature before using.

General Procedure for TfOH-Catalyzed Diacetoxylation of Alkenes Using AcO_2H. The solution of peracetic acid (1.0 M, 2 mmol) was added to a 10 mL glass vial charged with 1.0 mmol of aliphatic alkene and cooled with the aid of a water bath (for aromatic alkenes, cooled in an ice−water bath), followed by the addition of 1.0 M TfOH solution in glacial acetic acid (0.1 mmol). The resulting reaction mixture was stirred at room temperature for required time. The reaction mixture was concentrated by rotary evaporation, and the residue was used to determine the diastereoselectivity by NMR if applicable. The crude product was purified by column chromatography on silica gel using hexane and ethyl acetate as the eluent.

General Procedure for TfOH-Catalyzed Diacetoxylation of Alkenes Using *m*-CPBA. 3-Chloroperoxybenzoic acid (>70%) was added to the solution of alkene (1.0 mmol) in glacial acetic acid (2 mL) in a 10 mL glass vial cooled by a water bath (for aromatic alkenes, cooled in an ice−water bath), followed by the addition of 1.0 M TfOH solution in glacial acetic acid (0.1 mmol). The resulting reaction mixture was stirred at room temperature for required time, followed by the addition of 0.5 mL of acetic anhydride. This reaction mixture was

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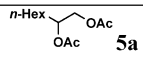
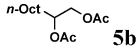
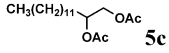
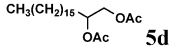
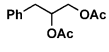
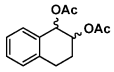
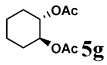
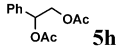
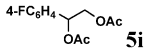
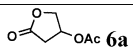
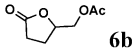
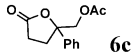
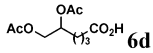
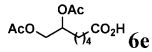
Table 2. TfOH-Catalyzed Diacetoxylation of Alkenes Using Peroxyacids as Oxidants[a]

Entry	Alkene	Product	Yield(%)[b,c]
1	1-octene	 **5a**	85(90)
2	1-decene	 **5b**	85(91)
3	1-tetradecene	 **5c**	89
4	1-octadecene	 **5d**	65(73)
5	allylbenzene	 **5e**	81[e](90)
6		 **5f**	91 [dr1/1]
7	cyclohexene	 **5g**	99 [dr12/1]
8	styrene	 **5h**	50(94)
9	4-F-styrene	 **5i**	54
10[d]	*trans*-stilbene	 **5j**	68 [dr2.6/1]
11[d]	*cis*-stilbene	 **5j**	56 [dr1.8/1]

[a]Conditions: 1.0 mmol of alkene, 2.0 mmol of AcO_2H [1 M in AcOH−Ac_2O (2.2/1 v/v)], room temperature. See Experimental Section for details. [b]Isolated yields. The yields in parentheses obtained from the reactions using 2.0 mmol of *m*-CPBA instead of AcO_2H in AcOH and then treated with Ac_2O. [c]dr refers to diastereoselectivity (syn/anti). [d]Carried out at 50 °C. [e]3 equiv of AcO_2H used.

Table 3. TfOH-Catalyzed Lactonization of Alkenes Using Peroxyacids as Oxidants[a]

Entry	Alkenoic acid	Lactone	Yield(%)[b]
1		 **6a**	99
2		 **6b**	97
3		 **6c**	66
4		 **6d**	80
5		 **6e**	67(100)

[a]Conditions: 1.0 mmol of alkene, 2.0 mmol of AcO_2H [1 M in AcOH−Ac_2O (2.2/1 v/v)], room temperature. See the Experimental Section for details. [b]Isolated yields. The yield in parentheses was obtained from the reaction using 2.0 mmol of *m*-CPBA instead of AcO_2H. The reaction mixture was treated with Ac_2O.

stirred for 12 h and concentrated by rotary evaporation and the residue was used to determine the diastereoselectivity by NMR if applicable. The residue was further diluted by dichloromethane and washed with 10% NaOH solution, dried over Na_2SO_4, concentrated, and purified by column chromatography on silica gel using hexane, ethyl acetate as the eluent.

*1,2-Diacetoxyoctane (**5a**).*[8] Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.08−5.04 (m, 1.0 H), 4.21 (dd, J = 12.0, 3.0 Hz, 1.0 H), 4.02 (dd, J = 12.0, 6.6 Hz, 1.0 H), 2.06 (s, 3.0 H), 2.05 (s, 3.0 H), 1.59−1.52 (m, 2.0 H), 1.30−1.25 (m, 8.0 H), 0.87 (t, J = 7.2 Hz, 3.0 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.6, 71.6, 65.1, 31.6, 30.7, 29.0, 25.0, 22.5, 21.1, 20.8, 14.0.

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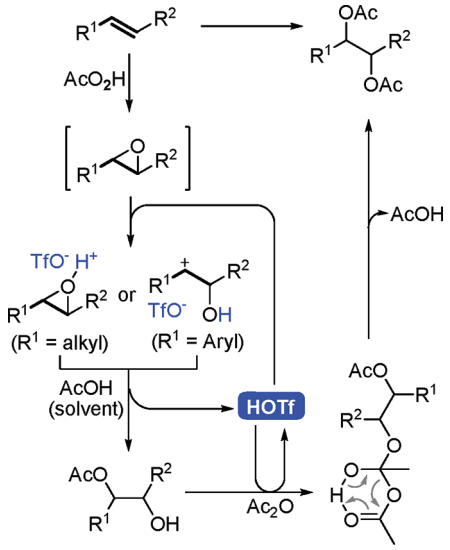
Scheme 3. Proposed Dual Catalytic Role of TfOH in the Diacetoxylation of Alkenes Using AcO_2H



*1,2-Diacetoxydecane (**5b**).*[9a] Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.06−5.05 (m, 1 H), 4.21 (dd, J = 3.0, 12.0 Hz), 4.02 (dd, J = 6.6, 11.4 Hz), 2.06 (s, 3 H), 2.05 (s, 3 H), 1.57−1.55 (m, 2 H), 1.30−1.25 (m, 12 H), 0.87 (t, J = 11.4 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.6, 71.6, 65.1, 31.8, 30.7, 29.4, 29.3, 29.1, 25.1, 22.6, 21.1, 20.8, 14.1.

*1,2-Diacetoxytetradecane (**5c**).* Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.05−5.04 (m, 1 H), 4.20 (dd, J = 3.0, 12.0 Hz), 4.00 (dd, J = 6.6, 11.4 Hz), 2.04 (s, 3 H), 2.04 (s, 3 H), 1.56−1.54 (m, 2 H), 1.27−1.23 (m, 20 H), 0.86 (t, J = 6.6 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.6, 77.2, 77.0, 76.8, 71.5, 65.1, 31.9, 30.6, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 25.1, 22.6, 21.0, 20.7, 14.1. HRMS (ESI): calcd for $C_{18}H_{34}NaO_4$ $[M + Na]^+$ 337.2349, found 337.2346. IR (neat): 2926, 2855, 1745, 1462, 1371, 1227, 1049 cm^{-1}.

*1,2-Diacetoxyoctadecane (**5d**).* The colorless oil slowly solidified to a hard white waxlike solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.08−5.04 (m, 1 H), 4.21 (dd, J = 3.0, 12.0 Hz), 4.02 (dd, J = 6.6, 12.0 Hz), 2.063 (s, 3 H), 2.058 (s, 3 H), 1.60−1.52 (m, 2 H), 1.30−1.25 (m, 28 H), 0.87 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.9, 170.7, 71.6, 65.1, 31.9, 30.7, 29.7, 29.7, 29.7(2C), 29.6(2C), 29.6, 29.5, 29.4, 29.4, 29.4, 25.1, 22.7, 21.1, 20.8, 14.1. HRMS (ESI): calcd for $C_{22}H_{42}NaO_4$ $[M + Na]^+$ 393.2975, found 393.2973. IR (neat): 3295, 2916, 2849, 1745, 1720, 1463, 1263 cm^{-1}.

*1,2-Diacetoxy-3-phenylpropane (**5e**).*[8] Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30−7.19 (m, 5H), 5.26 (ddd, J = 3.6, 6.6, 13.2 Hz, 1H), 4.23 (dd, J = 12.0, 3.6 Hz, 1H), 4.02 (dd, J = 12.6, 6.0 Hz, 1H), 2.93 (dd, J = 13.8, 7.2 Hz, 1H), 2.88 (dd, J = 13.8, 6.6 Hz, 1H), 2.07 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.7, 170.3, 136.2, 129.2, 128.5, 126.8, 77.2, 77.0, 76.8, 72.0, 64.2, 37.0, 20.9, 20.7.

*1,2-Diacetoxytetrahydronaphthalene (**5f**).*[8] (1:1 mixture of syn and anti). Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28−7.14 (m, 8 H), 6.18 (d, J = 3.0 Hz, 1 H), 6.07 (d, J = 6.0 Hz, 1.0 H), 5.25 (dt, J = 10.8, 3.6 Hz, 1 H), 5.18 (ddd, J = 9.2, 6.0, 3.3 Hz,1 H), 3.03 (dt, J = 16.8, 5.4 Hz,1 H), 2.95−2.90 (m, 3 H), 2.27−2.21 (m, 1 H), 2.20−2.15 (m, 1 H), 2.11 (s, 3.0 H), 2.10 (s, 3 H), 2.06 (s, 0.6 H), 2.05 (s, 3.0 H), 2.07−1.94 (m, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.6, 170.6, 170.4, 170.3, 136.6, 136.4, 132.7, 132.7, 130.0, 129.1, 128.8, 128.7, 128.6, 128.3, 126.5, 126.4, 71.4, 71.0, 70.1, 69.3, 27.1, 25.7, 24.9, 23.3, 21.2, 21.1, 21.1.

*anti-1,2-Diacetoxycyclohexane (**5g**).*[13] Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.81−4.76 (m, 2 H), 2.08−2.02 (m, 2 H), 2.01 (s, 6H), 1.72−1.70 (m, 2H), 1.39−1.24 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.5, 73.7, 30.1, 23.4, 21.1.

*1,2-Diacetoxy-3-phenylethane (**5h**).*[8] Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37−7.31 (m, 5H), 6.01 (dd, J = 8.4, 3.6 Hz, 1H), 4.33 (dd, J = 12.0, 3.6 Hz, 1H), 4.29 (dd, J = 8.4, 12.0 Hz, 1H), 2.12 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.7, 170.1, 136.5, 128.6, 128.6, 126.7, 73.3, 66.1, 21.1, 20.8.

*1,2-Diacetoxy-3-(4-fluorophenyl)ethane (**5i**).*[9a] Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36−7.33 (m, 2 H), 7.08−7.04 (m, 2 H), 5.98 (dd, J = 13.8, 4.2 Hz, 1 H), 4.30 (dd, J = 12.0, 4.2 Hz, 1H, 4.26 (dd, J = 12.0, 7.8 Hz, 1H), 2.11 (s, 3 H), 2.05 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.6, 170.0, 163.6, 161.9, 132.4, 132.4, 128.6, 128.6, 115.7, 115.6, 72.6, 65.9, 65.9, 21.1, 20.7.

*anti-1,2-Diacetoxy-1,2-diphenylethane (anti-**5j**).*[8] The colorless oil slowly solidified to a solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29−7.28 (m, 6 H), 7.20−7.19 (m, 4 H), 6.08 (s, 2 H), 2.01 (s, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.6, 134.0, 128.4, 128.1, 127.6, 76.4, 21.0.

*syn-1,2-Diacetoxy-1,2-diphenylethane (syn-**5j**).*[8] The colorless oil slowly solidified to a solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22−7.14 (m, 10 H), 6.05 (s, 2 H), 2.08 (s, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.8, 136.1, 128.4, 128.2, 127.5, 77.1, 21.0.

*3-Acetoxy-γ-butyrolactone (**6a**).*[10] Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.41−5.42 (m, 1 H), 4.49 (dd, J = 4.8, 11.4 Hz, 1 H), 4.35 (d, J = 10.8 Hz, 1 H), 2.84 (dd, J = 6.6, 18.0 Hz, 1 H), 2.60 (d, J = 18.0 Hz, 1 H), 2.08 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 174.5, 170.3, 73.0, 69.7, 34.5, 20.8.

*ω-Acetoxy-γ-pentanolactone (**6b**).*[8] Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.75−4.71 (m, 1 H), 4.30 (dd, J = 3, 12 Hz, 1 H), 4.13 (dd, J = 5.4, 12.6 Hz, 1 H), 2.62−2.52 (m, 2 H), 2.37−2.32 (m, 1 H), 2.09 (s, 3 H), 2.07−2.00 (m, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 176.5, 170.6, 77.2, 65.3, 28.1, 23.9, 20.9.

*ω-Acetoxyl-4-phenyl-γ-pentanolactone (**6c**).* Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40−7.33 (m, 5 H), 4.32 (d, J = 12 Hz, 1 H), 4.29 (d, J = 12 Hz, 1 H), 2.76−2.66 (m, 2 H), 2.58−2.52 (m, 1 H), 2.49−2.44 (m, 1 H), 2.08 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 175.9, 170.3, 139.8, 128.8, 128.5, 124.9, 86.7, 69.6, 31.2, 28.8, 20.7. HRMS (ESI): calcd for $C_{13}H_{15}O_4$ $[M + H]^+$ 235.0965, found 235.0962. IR (neat): 3545, 3474, 3062, 3031, 2957, 2924, 2854, 1790, 1743, 1450, 1326, 1254, 1049, 949, 767 cm^{-1}.

*5,6-Diacetoxyhexanoic Acid (**6d**).*[8] Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.10−5.06 (m, 1 H), 4.22 (dd, J = 12.0, 3.6 Hz, 1 H), 4.04 (dd, J = 12.0, 6.6 Hz, 1 H), 2.39 (t, J = 6.6 Hz, 2 H), 2.07 (s, 3 H), 2.06 (s, 3 H), 1.73−1.62 (m, 4 H).^{13}C NMR (150 MHz, $CDCl_3$): δ 178.5, 170.8, 170.7, 71.0, 64.9, 33.4, 30.0, 21.0, 20.8, 20.2.

*6,7-Diacetoxyheptanoic Acid (**6e**).*[8] Colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.09−5.05 (m, 1 H), 4.21 (dd, J = 12.0, 3.6 Hz, 1 H), 4.02 (dd, J = 12.0, 6.0 Hz, 1 H), 2.36 (t, J = 7.2 Hz, 1 H), 2.064 (s, 3 H), 2.058 (s, 3 H), 1.67−1.58 (m, 4 H), 1.41−1.36 (m, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 179.1, 170.8, 170.7, 71.2, 65.0, 33.6, 30.3, 24.5, 24.3, 21.0, 20.8.

■ ASSOCIATED CONTENT

Supporting Information

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

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