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Epoxidation of Olefins with a Silica-Supported Peracid

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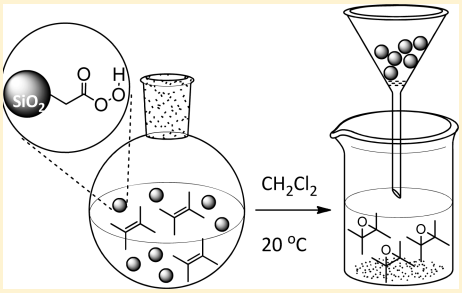
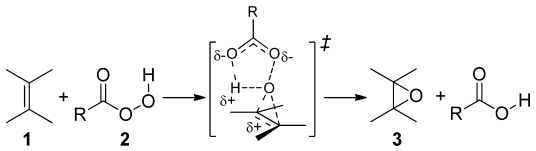
Supporting Information

ABSTRACT: Anhydrous [2-percarboxyethyl] functionalized silica (**2a**) is an advantageous oxidant for performing the epoxidation of olefins **1**. Epoxides **3** do not undergo the ring-opening reactions catalyzed by the acidic silica surface, except for particularly activated cases such as styrene oxide. The hydrophilic and acidic character of the silica surface does not interfere with the directing effects exerted by allylic H-bond acceptor substituents. The alkenes **1** carrying hydroxyl groups react with silica-supported peracid **2a** faster than unsubstituted alkenes, thus reversing the trend known for reactions with soluble peracids. These results are attributed to the H-bond interactions of substrate **1** with the silanol and carboxylic acid groups bonded to the silica surface.



The reaction of olefins **1** with organic peroxyacids **2** (Scheme 1), a classic procedure[1,2] for the preparation of epoxides **3**, is still widely used on both laboratory and industrial scales. The importance of epoxides **3** as versatile synthetic intermediates and commodity products[3] has prompted active research on alternative procedures for performing this reaction since some properties of organic peroxyacids, such as high price, risk of uncontrolled decomposition, and the low atom-economy of their oxygenation reactions, limit their use as oxidants.

Scheme 1. Epoxidation of Olefins 1 with Peracids 2



Supported organic peroxyacids are interesting alternatives for the oxygenation of organic substrates since the immobilization of peroxide on an inert solid matrix minimizes the explosion hazard, allows the design of continuous flow processes, and simplifies both the isolation of the reaction products and reagent recycling by suppressing neutralization and extraction operations for the separation of the carboxylic acid formed in the oxygen transfer step. In this context, [2-percarboxyethyl] functionalized silica (**2a**)[4] has proven to be a suitable reagent for performing the oxygenation of ketones and sulphides under a variety of reaction conditions.[5] The porous and rigid character of the silica support provides a large solid−liquid interface that facilitates the access of the substrate solution to the surface peroxydic ligands; however, the acidic character of the silica surface occasionally interferes and deviates the reaction course in relation to its homogeneous counterparts.[5] This fact is particularly relevant for epoxidation reactions since silanol and carboxylic acid ligands on the silica surface might efficiently promote the degradation of acid-sensitive epoxides **3**. The epoxidation of simple olefins **1** with silica-supported peracid **2a** has been reported[4c] by other authors in the preliminary screening of the reactivity of solid peracid **2a**. This precedent, the synthetic importance of epoxides **3** and the significant operative improvements provided by silica-supported peroxyacid **2a** in oxygenation reactions, prompted us to revise this reaction in depth with a view to broadening its synthetic application.

Herein we report the epoxidation of simple and substituted olefins **1** with anhydrous [2-percarboxyethyl] functionalized silica (**2a**). This procedure simplifies the isolation of epoxides **3**, which requires merely filtering the reaction mixture and evaporating the solvent. Solid oxidant **2a** can be recycled by treatment with 30% hydrogen peroxide in acid medium. The surface phenomena associated with the hydrophilic and acidic silica surface of solid peracid **2a** promote faster reaction rates for alkenols than for unsubstituted alkenes, unlike reactions with soluble peracids.

RESULTS AND DISCUSSION

[2-Percarboxyethyl] functionalized silica (**2a**) was prepared[4] by acid hydrolysis of [2-cyanoethyl] functionalized silica, obtained by a standard sol−gel method, followed by the treatment of the resulting [2-carboxyethyl] functionalized silica with 30% hydrogen peroxide in an acid medium (Scheme 2). Lyophilization of the solid reagent yielded a ca. 22−25% w/w hydrated material, which was dried under vacuum at room temperature until it reached a constant weight. ^{1}H NMR analysis, performed according to reported procedures,[6] and iodometric titration of silica-supported peracid **2a** showed loads of 2.5−3.5 mmol of organic ligands and 1.2−1.7 mmol of peracid per gram of hybrid material, respectively. Silica-

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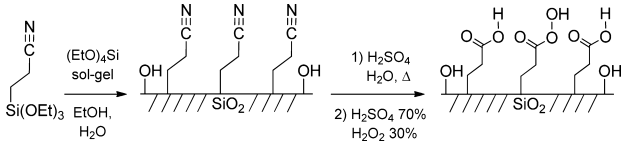
Scheme 2. Synthesis of [2-Percarboxyethyl] Functionalized Silica (2a)[4]



supported peracid **2a** can be stored at −20 °C for weeks with no noticeable loss of the peroxidic titer. Hydrated samples of solid peracid **2a** were prepared by adding the desired amount of water to the anhydrous solid and then allowing the mixture to equilibrate at 4 °C for 12 h.

Epoxidations were carried out at room temperature by adding anhydrous silica-supported peracid **2a** to a 0.03 M solution of substrate **1** in dichloromethane under stirring. The initial molar alkene:peracid **1**:**2a** ratio ranged between 1:2 and 1:3. Reactions were monitored by gas chromatography. Once the substrate conversion was complete, the mixture was filtered, the solid was thoroughly washed with dichloromethane, and the reaction product was isolated by evaporating the solvent under vacuum. The results are shown in Table 1.

The consumed silica-supported reagent was white, had a loose appearance in all cases, and showed loss of the peroxidic titer which corresponded to the oxygen-transfer performed to substrate **1**. Mass balances, which were determined by carrying out the reactions in the presence of adamantane as an internal standard, were correct in all cases, indicating that the silica surface did not retain epoxides **3** under these reaction conditions. Silica-supported peracid **2a** was recycled by treating the solid material with hydrogen peroxide in acid medium. After five cycles, the load of the peroxydic ligands on the silica surface was 0.8 mmol per gram of hybrid material.

The results show that anhydrous [2-percarboxyethyl] functionalized silica (**2a**) is an advantageous reagent for performing the epoxidation of olefins **1** since a simple filtration separates the reduced peroxide from the reaction product, unlike the neutralization and extraction operations required for homogeneous reactions using soluble organic peracids. Epoxides **3** (Table 1) did not undergo acid-catalyzed ring-opening reactions promoted by the silanol and carboxylic acid groups bonded to the silica surface under these reaction conditions.

The epoxidation of olefins **1** required an excess of solid oxidant **2a** to achieve the complete conversion of the substrate within the reaction periods reported in Table 1. In contrast, homogeneous reactions with *m*-chloroperbenzoic acid (MCPBA) (**2b**) required only an equimolar amount of oxidant under similar reaction conditions. The diminished reaction efficiency noted for the heterogeneous reactions is related to the restricted diffusion of the peroxyacid ligands bonded to silica nanoparticles if compared to soluble peracids.

The reactivity of olefins **1** toward silica-supported peracid **2a** follows the pattern described[7] for reactions with soluble peracids. For instance, terminal olefins 1-hexene (**1f**) and allylbenzene (**1g**) and olefins carrying electron-withdrawing substituents such as 2-cyclohexenyl acetate (**1l**) and 2-hexenyl acetate (**1o**) required 3 equiv of supported peracid **2a** to achieve the complete conversion of substrates, while a 2-fold excess sufficed for internal and unsubstituted olefins, such as cyclohexene (**1a**) and *cis*-2-heptene (**1b**) (Table 1). The acid-catalyzed ring opening of epoxides **3** became competitive for highly acid-sensitive epoxides **3**. Hence, epoxidation of styrene (**1q**) and *cis*-stilbene (**1r**) led to low substrate conversions and products derived from acid-catalyzed ring opening and overoxidation that remained adsorbed on the silica surface.

The hydrophilic character of the silica surface surrounding the peroxydic ligands in **2a** did not interfere with the directing effects exerted by allylic hydroxy groups on the diastereoselectivity of the reaction. Thus, epoxidation of 2-cyclohexenol

Table 1. Epoxidation of Olefins 1 with [2-Percarboxyethyl] Functionalized Silica (2a)[a]

Run	Substrate	Time (h)	(±)Product	Yield (%)[b]
1	**1a**	1	**3a**	>99
2	**1b**	8	**3b**	99
3	**1c**	8	**3c**	95
4	**1d**	1	**3d**	95[c]
5	**1e**	1	**3e**	98
6	**1f**	8	**3f**	95[d]
7	**1g**	8	**3g**	96[d]
8	**1h**	1	**3h**	>99[e]
9	**1i**	1	**3i**	>99[f]
10	**1j**	2	**3j**	>99
11	**1k**	1	**3k**	>99
12	**1l**	8	**3l**	95[d,f]
13	**1m**	1	**3m**	>99[f]
14	**1n**	8	**3n**	99[f]
15	**1o**	8	**3o**	94[d]
16	**1p**	8	**3p**	96

[a]Reactions in dichloromethane with anhydrous **2a** at room temperature, with an initial substrate concentration 0.03 M and an initial molar alkene/peracid ratio of 1:2. [b]Epoxides were the only reaction products. [c]Only the *exo* isomer was formed. [d]The initial molar alkene/peracid ratio was 1:3. [e]Only the *sin* isomer was formed. [f]50:50 mixture of isomers.

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(**1h**) with silica-supported peracid **2a** led exclusively to the corresponding *syn*-epoxide **3h**, which is in agreement with the results reported for homogeneous reactions with soluble organic peracids.[8]

The most significant feature of the results offered in Table 1 is the enhanced reaction efficiency observed for the olefins **1** carrying hydroxy substituents. Noteworthily, terminal olefin 5-hexen-1-ol (**1k**) (entry 11, Table 1) reacted with silica-supported peracid **2a** as efficiently as unsubstituted internal olefins, such as cyclohexene (**1a**) or norbornene (**1d**) (entries 1 and 3, Table 1). These results cannot be attributed to the directing effects exerted by the hydroxy group on the approaching peracid since only allylic and homoallylic H-bond donor substituents are known to fulfill the geometric requirements for this type of interaction.[8]

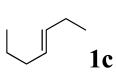
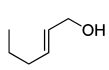
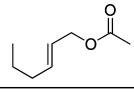
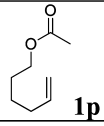
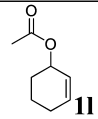
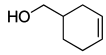
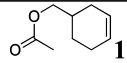
The relative reaction rates for distinctly substituted olefins toward anhydrous silica-supported peracid **2a** and MCPBA (**2b**) were ascertained in competitive experiments, which were carried out by adding either silica-supported peracid **2a** or an aliquot of a 0.1 M dichloromethane solution of MCPBA (**2b**) to a dichloromethane solution containing two competing substrates and adamantane as an internal standard. The initial molar alkene/alkenol/peracid or alkene/alkenyl ester/peracid ratios were 1:1:1 in all cases. The reactions were carried out at room temperature for 24 h. Homogeneous reactions were directly analyzed by gas chromatography. Heterogeneous reaction mixtures were filtered, the solid was thoroughly washed with dichloromethane in order to completely desorb any organic compound on the silica surface, and the filtrate was analyzed by gas chromatography. Relative reaction rates were determined by the integration of the chromatographic peaks corresponding to the substrates and the internal standard. Unsubstituted alkenes were taken as a reference for each triad of substrates and each peracid. Competition experiments were performed at least three times for each pair of substrates. The results are collected in Table 2.

The relative reaction rates found for the epoxidation of alkenes **1** with MCPBA (**2b**) (Table 2) follow the expected trend[2,7] of alkenyl ester < alkenol < alkene in all cases, in agreement with the inductive deactivation of the C=C double bond exerted by acetoxy (σ_I = 0.38)[9] and hydroxy (σ_I = 0.24)[9] substituents. Inductive deactivation decreases as the distance between the C=C double bond and the substituent increases, and accordingly, the relative reaction rates found for cyclohexene (**1a**), 2-cyclohexenol (**1h**), and 2-cyclohexenylacetate (**1l**) were 1, 0.33, and 0.03, respectively (entry 6, Table 2), and they were 1, 0.71 and 0.46, respectively, for cyclohexene (**1a**), 3-cyclohexenylmethanol (**1i**) and 3-cyclohexenylmethyl acetate (**1m**) (entry 8, Table 2).

Reactions of alkenes and alkenols with silica-supported peracid **2a** follow a reverse trend, with kinetic factors ranging between 8.33 and 4.54 for the pairs 2-cyclohexenol (**1h**)/cyclohexene (**1a**) and 5-hexen-1-ol (**1k**)/1-hexene (**1f**), respectively (entries 5 and 3, Table 2). Alkenes **2** carrying acetoxy substituents did not show anomalies in relation to homogeneous reactions, and the same may be said of the dependence of inductive deactivation on the distance between functional groups (Table 2).

These results can be interpreted in terms of a stronger adsorption of alkenols onto the hydrophilic silica surface of solid peracid **2a** in relation to simple olefins or alkenyl esters. This fact was ascertained by adding 25 mg of anhydrous 3-carboxypropyl functionalized silica (2.8 mmol per gram) to 3 mL of a 0.01 M dichloromethane solution of cyclohexene (**1a**) and 2-cyclohexenol (**1h**), and 0.015 M of adamantane as an internal standard at room temperature under stirring. The gas chromatography analysis of the filtered solution showed a 41% depletion of 2-cyclohexenol (**1h**) from the supernatant solution, while the concentration of cyclohexene (**1a**) remained invariable.

Table 2. Relative Reaction Rates for the Epoxidation of Alkenes 1 towards MCPBA (2b) and [2-Percarboxyethyl] Functionalized Silica (2a)[a]

Run	2	 **1c**	 **1j**	 **1o**
1	**2a**	1	7.56	0.03
2	**2b**	1	0.40	0.03
Run	**2**	 **1f**	 **1k**	 **1p**
3	**2a**	1	4.54	0.12
4	**2b**	1	0.62	0.41
Run	**2**	 **1a**	 **1h**	 **1l**
5	**2a**	1	8.33	0.08
6	**2b**	1	0.33	0.03
Run	**2**	 **1a**	 **1i**	 **1m**
7	**2a**	1	8.80	0.46
8	**2b**	1	0.71	0.46

[a]Competitive reactions were carried out for alkene/alkenol or alkene/alkenyl ester pairs in the presence of adamantane as an internal standard with an initial molar ratio for substrates and peracid of 1:1:1 in all cases. The unsubstituted alkene was taken as a reference for each triad of substrates and for each peracid; the values for the different sets of experiments are not comparable.

However, large adsorption equilibrium constants do not necessarily imply a kinetic advantage for alkenols in relation to alkenes. In fact, the silanol and carboxylic acid groups on the silica surface are the preferential adsorption sites for H-bond acceptor substrates since they are stronger acids (pK_a = 6.8[10] and 4−5, respectively) than peroxyacids (pK_a = 7.6[11]), and the strong H-bonding interactions of these ligands with the substrate would actually diminish its opportunities to collide with reactive surface peroxydic ligands. The experimental results then suggest that the adsorbed alkenol migrates from the initial adsorption site to adjacent acidic ligands through successive H-bonding shifts without leaving the active surface, driven by thermal activation or collisions with the solvent.[12]

CONCLUSIONS

[2-Percarboxyethyl] functionalized silica (**2a**) reacts efficiently with alkenes **1** to give the corresponding epoxides **3**, which can be isolated by filtering the reaction mixture and evaporating the solvent. Epoxides **3** do not undergo significant ring-opening reactions catalyzed by the acidic silica surface, except for particularly acid-sensitive cases, such as styrene oxide **3q**. The alkenes **1** carrying an H-bond acceptor hydroxyl group react with solid peracid **2a** faster than simple olefins, unlike the reactivity trend known for soluble peracids. This kinetic effect is

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attributed to interferences of surface phenomena on the reaction course. Silica-supported peracid **2a** is recyclable by treating the consumed reagent with 30% hydrogen peroxide in acid medium.

EXPERIMENTAL SECTION

General. Reagents and solvents were purified following standard procedures.[13] Alkenes **1** were commercial, except alkenyl acetates, which were prepared by standard procedures. The glassware used in the reactions with hydrogen peroxide was carefully cleaned and washed before use with a solution of EDTA in ultrapure water (0.25 g L^{-1}) to remove any traces of metals. Commercial 65−70% MCPBA (**2b**) was purified by treatment with an aqueous buffer solution of KH_2PO_4/K_2HPO_4 with pH 7.5. The solid was filtered and recrystallized from a 1:3 diethyl ether/*n*-hexane mixture to yield 99.9% MCPBA (**2b**), as shown by iodometric titration.

[2-Percarboxyethyl] Functionalized Silica (2a). A suspension of 3 g of [2-carboxyethyl] functionalized silica (2.6 mmol g^{-1}) in 7.5 mL of 70% H_2SO_4 was allowed to stir at 5 °C for 30 min. Then, 2.5 mL of 30% hydrogen peroxide was added at once, and the mixture was allowed to react at 0 °C under stirring for 6 h. The solid was filtered and washed with cold bidistilled water until the filtrate showed a negative peroxide test. The solid was dried under vacuum at room temperature until constant weight. Standard iodometric titration determined a peroxide content of 1.2 mmol g^{-1} of material.

Oxidation of Alkenes 1 with Silica-Supported Peracid 2a. General Procedure. To a stirred 0.03 M solution of 2-cyclohexenol **1h** (20 mL, 0.6 mmol) in dichloromethane, at room temperature was added 1.0 g of anhydrous solid peracid **2a** (1.2 mmol peracid g^{-1}, 1.2 mmol) at once. The reaction was stirred at room temperature for 1 h and was monitored by gas chromatography by withdrawing, filtering, and analyzing 0.1 mL aliquots at regular times. Once the reaction was complete, the mixture was filtered, and the solid was thoroughly washed with dichloromethane. The organic solution was treated with anhydrous magnesium sulfate, the solvent was evaporated under vacuum, and the residue was dissolved in deuterochloroform and analyzed by ^1H and ^{13}C NMR.

Competitive Experiments. General Procedure. To 3 mL of a 0.01 M dichloromethane solution of **1a** and **1h** and 0.005 M of adamantane, thermostatted at 20 °C was added either 25 mg of solid peracid **2a** (1.2 mmol g^{-1}, 0.03 mmol) or 0.3 mL of a thermostatted 0.1 M dichloromethane solution of MCPBA (**2b**). The reaction mixture was stirred for 6 h. The heterogeneous reaction mixture was filtered, the solid was thoroughly washed with dichloromethane, and the organic solution was analyzed by gas chromatography. For the homogeneous reaction, the solution was directly analyzed by gas chromatography. Substrate conversions were obtained from the peak areas of the starting materials and the internal standard.

Cyclohexene Oxide (3a) [286-20-4]. ^1H NMR (300 MHz, $CDCl_3$) δ 1.1−1.3 (2H, m), 1.4−1.5 (2H, m), 1.7−1.9 (2H, m), 1.9−2.0 (2H, m), 3.1 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4, 24.4, 52.2. EM (EI^+, 70 eV): *m*/*z* (rel abund) 39 (33), 41 (50), 42 (47), 54 (35), 55 (31), 57 (24), 69 (27), 70 (18), 83 (100), 97 (15), 98 (4, $[M^{\bullet+}]$).

(*Z*)-3-Heptene Oxide (3b) [56052-94-9]. ^1H NMR (300 MHz, $CDCl_3$) δ 1.0−1.2 (m, 6H), 1.4−1.7 (m, 6H), 2.8−3.0 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 10.5, 14.0, 19,8, 21.0, 29.6, 57.3, 58.5. EM (EI^+, 70 eV): *m*/*z* (rel abund) 57 (100), 67 (14), 72 (87), 81 (3), 85 (41), 99 (13), 114 (1, $[M^{\bullet+}]$).

(*E*)-3-Heptene Oxide (3c) [56052-95-0]. ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (3H, dt, J_1 = 2,6 Hz, J_2 = unresolved), 0.95 (3H, t, J = 7.5 Hz), 1.3−1.6 (6H, m), 2.6−2.7 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.8, 13.8, 19,3, 25.1, 34.0, 58.5, 60.0. EM (EI^+, 70 eV): *m*/*z* (rel abund) 57 (100), 67 (14), 72 (90), 81 (4), 85 (37), 99 (14), 114 (1, $[M^{\bullet+}]$).

***exo*-Norbornene Oxide (3d) [3146-39-2].** ^1H NMR (300 MHz, $CDCl_3$) δ 0.7 (1H, d), 1.1−1.2 (2H, m), 1.3 (1H, m), 1.4 (2H, m), 2.4 (2H, s), 3.1 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.0, 26.2, 36.6, 51.5. EM (EI^+, 70 eV): *m*/*z* (rel abund) 54 (42), 67 (37), 79 (75), 81 (100), 95 (17), 109 (5), 110 (3, $[M^{\bullet+}]$).

(*Z*)-3-Methylpentene Oxide (3e) [1447-39-8]. ^1H NMR (300 MHz, $CDCl_3$) δ 0.9 (3H, t, J = 7.5 Hz), 1.2 (3H, s), 1.3 (3H, d, J = 5.5 Hz), 1.5 (1H, dq, J_1 = 7.5 Hz, J_2 = 13.8 Hz), 1.6 (1H, dq, J_1 = 7.5 Hz, J_2 = 13.8 Hz), 2.9 (1H, q, J = 5.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.2, 14.1, 15.8, 31.3, 59.0, 62.0. EM (EI^+, 70 eV): *m*/*z* (rel abund) 41 (100), 43 (63), 45 (22), 56 (47), 72 (71), 85 (2), 100 (1, $[M^{\bullet+}]$).

1-Hexene Oxide (3f) [592-41-6]. ^1H NMR (300 MHz, $CDCl_3$): δ 0.9 (3H, t, J = 7 Hz), 1.3−1.6 (6H, m), 2.5 (1H, dd, J_1 = 2.8 Hz, J_2 = 4.9 Hz), 2.8 (1H, dd, J_1 = 4.1 Hz, J_2 = 4.9 Hz), 2.9 (1H, d sext, J_1 = 2.8 Hz, J_2 = 4.0 Hz, J_3 = J_4 = 5.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.4, 28.0, 32.0, 47.3, 52.7. EM (EI^+, 70 eV): *m*/*z* (rel abund) 39 (18), 41 (42), 42 (43), 55 (39), 58 (33), 71 (100), 85 (7), 99 (1), 100 (0, $[M^{\bullet+}]$).

2-Phenylpropene Oxide (3g) [4436-24-2]. ^1H NMR (300 MHz, $CDCl_3$) δ 2.5 (1H, dd, J_1 = 2.7 Hz, J_2 = 5.0 Hz), 2.7−2.9 (3H, m), 3.1 (1H, dsext, J_1 = 2.7 Hz, J_2 = 3.9 Hz, J_3 = J_4 = 5.5 Hz), 7.1−7.2 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.6, 46.7, 52.3, 126.5, 128.4, 128.8, 137.0. EM (EI^+, 70 eV): *m*/*z* (rel abund) 44 (30), 50 (12), 65 (25), 78 (21), 91 (100), 104 (35), 117 (13), 134 (55, $[M^{\bullet+}]$).

1-Hydroxy-2-cyclohexene Oxide (3h) [1192-78-5]. ^1H NMR (300 MHz, $CDCl_3$) δ 1.2−1.3 (2H, m), 1.4−1.6 (2H, m), 1.7−1.9 (2H, m), 2.0 (1H, broad s, OH), 3.3−3.4 (2H, m), 4.0 (1H, ddd, J_1 = 2.9 Hz, J_2 = 4.7 Hz, J_3 = 7.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.1, 23.1, 28.9, 55.3, 55.4, 67.0. EM (EI^+, 70 eV): *m*/*z* (rel abund) 41 (20), 57 (74), 58 (37), 60 (7), 70 (100), 83 (4), 95 (6), 114 (0, $[M^{\bullet+}]$).

1-Hydroxymethyl-3-cyclohexene Oxide (3i) [767-11-3]. Mixture of isomers 50:50. ^1H NMR (300 MHz, $CDCl_3$) δ 0.9−1.2 (1H, m), 1.3−1.9 (6H, m), 2.0−2.2 (2H, m), 3.1−3.2 (2H, m), 3.3−3.5 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8, 23.0, 23.6, 24.5, 27.0, 27.9, 32.5, 35.2, 51.4, 51.9, 52.7, 52.8, 67.3, 67.6; EM (EI^+, 70 eV): *m*/*z* (rel abund) *isomer 1* 41(96), 55(54), 57 (50), 67 (75), 69 (54), 79 (56), 84 (93), 97(100), 109(11), 128 (2,$[M^{\bullet+}]$); *isomer 2* 41 (100), 55(57), 57(60), 67 (73), 69 (51), 79 (64), 84 (93), 97 (100), 109 (9), 127 (1) 128 (1,$[M^{\bullet+}]$).

(*E*)-1-Hydroxy-5-hexene Oxide (3j) [106498-75-3]. ^1H NMR (300 MHz, $CDCl_3$) δ 0.9 (3H, t, J = 7.3 Hz), 1.4−1.6 (5H, m), 2.9−3.0 (2H, m), 3.6 (1H, dd, J_1 = 4.6 Hz, J_2 = 12.7 Hz), 3.9 (1H, dd, J_1 = 2.4 Hz, J_2 = 12.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 19.1, 33.4, 56.2, 58.8, 61.7. EM (EI^+, 70 eV): *m*/*z* (rel abund) 41 (40), 43 (46), 55 (100), 57 (31), 73 (31), 83 (4), 98 (1), 116 (0, $[M^{\bullet+}]$).

1-Hydroxy-5-hexene Oxide (3k) [21915-57-1]. ^1H NMR (300 MHz, $CDCl_3$) δ 1.4−1.7 (6H, m), 2.5 (1H, dd, J_1 = 2.8 Hz, J_2 = 4.9 Hz), 2.8 (1H, d, J = 4.1 Hz), 2.9−3.0 (1H, m), 3.7 (2H, t, J = 6.2 Hz), 6.1 (1H, broad s, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.2, 32.0, 32.1, 47.1, 52.4, 62.5. EM (EI^+, 70 eV): *m*/*z* (rel abund) 41 (28), 43 (15), 55 (9), 57 (26), 67 (20), 85 (100), 105 (2), 116 (1, $[M^{\bullet+}]$).

1-Methylcarbonyloxy-2-cyclohexene Oxide (3l) [84414-68-6]. Mixture of isomers 60:40. ^1H NMR (300 MHz, $CDCl_3$) δ 1.1−1.6 (6.7H, m), 1.7−1.9 (4H, m), 1.9−2.0 (1.5H, m), 2.1 (5.2H, ds), 3.0 (1H, d, J = 3.6 Hz), 3.1−3.2 (1H, m), 3.2−3.3 (1.3H, m), 5.0(1H, t, J = 7 Hz), 5.1 (1H, ddd, J_1 = 1.7 Hz, J_2 = 5.1 Hz, J_3 = 9.1 Hz); ^{13}C NMR (75 MHz, CDCl3) δ *major isomer* 14.4, 21.1, 23.6, 25.7, 52.5, 53.3, 68.0, 170.1, *minor isomer* 19.3, 21.1, 22.5, 24.4, 52.8, 54.2, 70.8, 170.8. EM (EI^+, 70 eV): *m*/*z* (rel abund) *major isomer* 43 (100), 55 (18), 68 (18), 70 (54), 86 (9), 96 (17), 112 (21), 156 (0, $[M^{\bullet+}]$); *minor isomer* 43 (100), 55 (14), 67 (18), 70 (61), 86 (5), 96 (19), 112 (24), 156 (0, $[M^{\bullet+}]$).

1-Methylcarbonyloxymethyl-3-cyclohexene Oxide (3m) [75228-31-8]. Mixture of isomers 50:50. ^1H NMR (300 MHz, $CDCl_3$) δ 0.9−1.2 (1.30 H, m), 1.3−1.9 (5H, m), 2.0−2.1 (4.5H, s), 2.1−2.2 (1.1H, m), 3.1−3.2 (2H, m), 3.82 (1H, d, J = 6.0 Hz), 3.86 (1H, dd, J_1 = 2.2 Hz, J_2 = 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.8, 21.0, 22.8, 23.6, 24.5, 27.0, 28.1, 29.3, 32.1, 51.0, 51.6, 52.3, 52.4, 68.3, 68.5, 171.07, 171.09. EM (EI^+, 70 eV): *m*/*z* (rel abund) *isomer 1* 43 (100), 55 (22), 67 (44), 81 (85), 95 (33), 110 (39), 127 (26), 170 (0, $[M^{\bullet+}]$); *isomer 2* 43 (100), 55 (21), 67 (43), 81 (81), 95 (37), 110 (43), 127 (23), 170 (0, $[M^{\bullet+}]$).

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1-Methoxycarbonyl-2-cyclohexene Oxide (3n) [864724-47-0]. Mixture of isomers 60:40. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.3−1.4 (1.2H, m), 1.5−1.6 (1.4H, m), 1.6−2.0 (5.4H, m), 2.0−2.2 (3.8H, m), 2.4−2.5 (1H,m), 3.0−3.1 (2.3H, m), 3.1−3.2 (1H, m), 3.60 (1.9H, s), 3.61 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ *major isomer* 22.7, 22.8, 27.1, 35.6, 51.6, 51.7, 52.1, 175.8, *minor isomer* 20.9, 23.9, 26.2, 37.7, 50.6, 51.3, 51.7, 52.1, 175.2. EM (EI^+, 70 eV): *m*/*z* (rel abund) *major isomer* 67 (27), 70 (28), 79 (30), 87 (19), 97 (100), 100 (24), 113 (7), 125 (26), 128 (7), 137 (3), 156 (0.5, [$M^{\bullet+}$]); *minor isomer* 67 (26), 70 (29), 81 (41), 87 (19), 97 (100), 100(21), 113 (7), 128 (6), 141 (1), 156 (0.7, [$M^{\bullet+}$]).

(*E*)-1-Methylcarbonyloxy-2-hexene Oxide (3o) [92315-15-6]. ^{1}H NMR ($CDCl_3$) δ 0.9 (3H, t, J = 7.3 Hz), 1.3−1.5 (4H, m), 2.0 (3H, s), 2.8 (1H, m), 2.9 (1H, m), 3.8 (1H, dd, J_1 = 6.3 Hz, J_2 = 12.2 Hz), 4.3 (1H, dd, J_1 = 3.1 Hz, J_2 = 12.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 19.0, 20.6, 33.3, 55.0, 56.2, 64.6, 170.6. EM (EI^+, 70 eV): *m*/*z* (rel abund) 43 (100), 55 (11), 57 (8), 73 (3), 86 (6), 99 (1), 115 (9), 129 (1), 158 (0, [$M^{\bullet+}$]).

1-Methylcarbonyloxy-5-hexene Oxide (3p) [107127-73-1]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.4−1.7 (6H, m), 2.0 (3H, s), 2.4 (1H, ddd, J_1 = 0.9 Hz, J_2 = 2.7 Hz, J_3 = 4.9 Hz), 2.7 (1H, ddd, J_1 = 0.9 Hz, J_2 = 4.5 Hz, J_3 = 4.5 Hz), 2.8−2.9 (1H, m), 4.0 (2H, td, J_1 = 0.81 Hz, J_2 = 6.43 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9, 22.4, 28.3, 32.0, 46.9, 52.0, 64.2, 171.1. EM (EI^+, 70 eV): *m*/*z* (rel abund) 43 (100), 55 (20), 67 (39), 85 (50), 97 (32), 115 (1), 158 (0, [$M^{\bullet+}$]).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of the reaction products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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