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Epoxidation of Olefins with a Silica-Supported Peracid in Supercritical Carbon Dioxide under Flow Conditions

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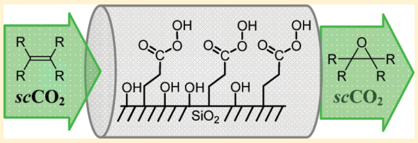
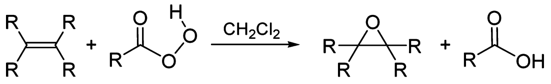
Ⓢ *Supporting Information*

ABSTRACT: Anhydrous 2-percarboxyethyl-functionalized silica (**2b**), a recyclable supported peracid, is a suitable reagent to perform the epoxidation of alkenes **1** in supercritical carbon dioxide at 250 bar and 40 °C under flow conditions. This procedure simplifies the isolation of the reaction products and uses only carbon dioxide as a solvent under mild conditions. The solid reagent **2b** can be easily recycled by a reaction with 30% hydrogen peroxide in an acid medium.



INTRODUCTION

Epoxides are versatile intermediates in organic synthesis and important commodity products which are produced at scales ranging from millions of tons to a few grams per year.[1] The reaction of alkenes **1** with organic peroxyacids **2a** (eq 1)[2] is still



1 **2a** R = alkyl, aryl **3** (1)

widely used for the production of epoxides **3** on both the industrial and laboratory scales, despite certain disadvantages such as the shock sensitivity of organic peroxyacids **2a**, the low atom economy of the process, the use of chlorinated or aromatic solvents as a reaction medium, and the formation of 1 equiv of carboxylic acid as a byproduct, which has to be separated from the acid-sensitive epoxide **3** by neutralization and extraction with organic solvents.

The synthetic importance of this transformation has prompted research into alternative methods[3] for the safe and environmentally benign production of epoxides **3** from olefins **1**. Use of supported organic peroxyacids[4,5] is a suitable approach to improve the reaction conditions, as immobilization on solid supports minimizes the risk of explosion of the peroxide and simplifies the removal of the carboxylic acid from the reaction products. This process could be further improved by performing the reaction under flow conditions and by avoiding the use of chlorinated or aromatic solvents.

Supercritical carbon dioxide (*sc*CO_2) is a convenient medium in which to perform heterogeneous reactions[6] with supported reagents and catalysts under flow conditions, given its adjustable solvating power, excellent transport properties, readily accessible critical conditions (T_c = 31.0 °C, P_c = 73.8 bar), benign character, low cost, and the existence of a technology platform to use *sc*CO_2 in large-scale processes. However, the epoxidation of olefins under flow conditions in this medium has not been described up to now.

This report describes the use of supercritical carbon dioxide (*sc*CO_2) as a reaction medium for the epoxidation of olefins **1** with recyclable 2-percarboxyethyl-functionalized silica (**2b**)[4] under flow conditions. The reaction works efficiently for simple, substituted olefins **1** and enables good yields of the corresponding epoxides **3**. The procedure described herein replaces organic solvents with *sc*CO_2 and simplifies the isolation of epoxides **3** to a simple depressurization of the flowing *sc*CO_2 solution. The process is not suitable for those olefins **1** carrying strong H-bond donor/acceptor substituents, such as alkenyl alcohols. This report also describes an optimized procedure for the preparation of silica-supported peracid **2b**, which avoids the use of highly concentrated hydrogen peroxide.

RESULTS AND DISCUSSION

2-Percarboxyethyl-functionalized silica (**2b**)was prepared[4,5a,b] by acid hydrolysis of 2-cyanoethyl-functionalized silica, obtained by a standard sol−gel procedure, followed by treatment of the resulting 2-carboxyethyl-functionalized silica with 30% hydrogen peroxide in an acid medium (Scheme 1).

Scheme 1. Synthesis of the Supported Peracid 2b[4]

$$(EtO)_3Si(CH_2)_2CN \xrightarrow[\substack{EtOH\\H_2O}]{(EtO)_4Si} \mathbf{[SiO_2]}(CH_2)_2CN \xrightarrow[\substack{2)\ 30\%\ H_2O_2\\H_2SO_4}]{\substack{1)\ H_2SO_4\\H_2O,\ \Delta}} \mathbf{[SiO_2]}(CH_2)_2CO_3H$$

The preparation of the silica-supported peracid **2b** described herein (see the Experimental Section) improves upon previously reported procedures,[4,5] which required less available and hazardous 70% solutions of hydrogen peroxide. Solid peroxidic reagent **2b** was dried under vacuum at room temperature until a constant weight was achieved. An analysis of the hybrid material by conventional ^1H NMR following a

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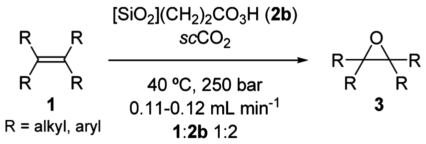
reported procedure[7] and iodometric titration, showed loads of 2.6 mmol of organic ligands and 1.2 mmol of peroxidic ligands per gram of hybrid material, respectively. Silica-supported peracid **2b** was stored at −20 °C for weeks with no noticeable loss of peroxidic titer.

Oxidations were carried out by flowing *sc*CO_2 (0.10−0.12 mL *sc*CO_2 min^{-1}) at 250 bar and 40 °C for 2 h through the loop of a Rheodyne valve containing substrate **1** and then through a column packed with anhydrous reagent **2b** (initial molar ratios alkene **1**:peracid **2b** 1:2 or 1:3) (eq 2). The system was depressurized through a micrometric valve, and the reaction product was collected in a trap cooled to −78 °C. The residue, which was obtained after gently heating the trap, was dissolved in dichloromethane and analyzed by gas chromatography. The reaction products were identified by gas chromatography/mass spectrometry and by ^1H and ^{13}C NMR analyses. The results are shown in Table 1.

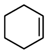
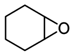
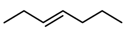
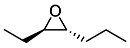
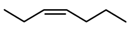
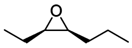
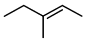
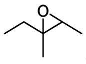
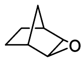
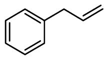
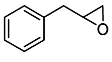
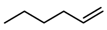
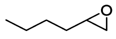
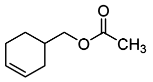
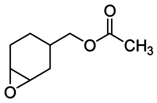
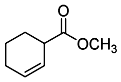
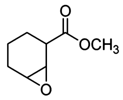
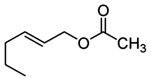
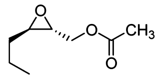
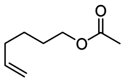
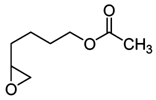
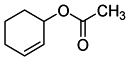
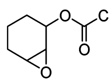
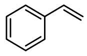
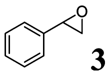


(2)

The silica-supported reagent recovered from the column was white and had a loose appearance in all cases. Iodometric titration of the consumed reagent showed loss of peroxidic titer, which corresponded to the oxygen transfer performed on the substrate. The mass balances for alkenes **1a**−**l**, 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 the corresponding epoxides **3a**−**l** under these conditions. Silica-supported peracid **2b** was recycled by treating the consumed solid material with 30% hydrogen peroxide in an acid medium, following the procedure described in the Experimental Section. After five cycles, the load of peroxidic ligands on the silica surface was 0.8 mmol per gram of hybrid material, indicating a loss of ca. 30% of organic ligands.

The results reveal that 2-percarboxyethyl-functionalized silica (**2b**)[4] is a superior reagent for the epoxidation of simple, substituted olefins **1** in *sc*CO_2 under flow conditions (Table 1). One interesting improvement in relation to reactions with soluble peracids is that epoxides **3** (Table 1) did not undergo acid-catalyzed side reactions promoted by the acidic silanol and carboxylic acid groups covering the silica surface. This result is most significant, as it is known that *sc*CO_2's low solvating ability enhances acid−base interactions.[6] A key factor for the success of the reaction was the anhydrous character of the supported peracid **2b**. The use of 20−25% hydrated silica-supported peracid **2b** led to low substrate conversions and extensive ring opening of epoxides **3** in all cases. These results indicate that the hydration layer on the silica surface poses a barrier for the interation of hydrophobic substrates **1** with the surface peroxidic moieties and that the water molecules coordinated to the surface silanol and carboxylic acid groups are sufficiently nucleophilic to perform the acid-catalyzed ring opening of epoxides **3**. The control experiments carried out with an initial 2:1 molar ratio of cyclohexene (**1a**) to peracid **2b** led to the complete consumption of the peracid **2b**, demonstrating that the high diffusivity and low viscosity of *sc*CO_2 allow the substrate to reach all the peroxidic ligands on the silica surface.

Table 1. Oxidation of Alkenes 1 with [SiO_2]-CH_2CH_2COOOH (2b) in *sc*CO_2 under Flow Conditions[a]

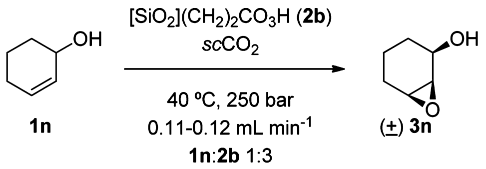
Run	Substrate	Product	Yield[b]
1	 **1a**	 **3a**	>99
2	 **1b**	 **3b**	>99
3	 **1c**	 **3c**	96
4	 **1d**	 **3d**	>99
5	 **1e**	 **3e**	>99
6	 **1f**	 **3f**	97[c]
7	 **1g**	 **3g**	>99[c]
8	 **1h**	 **3h**	97[d]
9	 **1i**	 **3i**	>99[d]
10	 **1j**	 **3j**	99[c]
11	 **1k**	 **3k**	>99[c]
12	 **1l**	 **3l**	>99[c,d]
13	 **1m**	 **3m**	--[e]

[a] Reactions in *sc*CO_2 at 250 bar, 40 °C and flow rate 0.11−0.12 mL *sc*CO_2 min^{-1}, with anhydrous **2b** (1.2 mmol of peracid g^{-1}), and molar ratio alkene **1**:peracid **2b** 1:2. Substrate conversion was complete in all the cases except where noted. [b] Determined by GC analysis of the reaction mixtures; mass balance >98% in all the cases. [c] Initial molar ratio alkene **1**:peracid **2b** 1:3. [d] Syn:anti ratio 50:50. [e] Substrate conversion <10%.

The results provided in Table 1 evidence the distinct reactivity of olefins **1** toward electrophilic oxidant **2b**.[8] Thus, the quantitative epoxidation of terminal olefins 3-phenylpropene (**1f**) and 1-hexene (**1g**) (entries 6 and 7, Table 1) required a 3-fold excess of peracid **2b**, while a 2-fold excess sufficed for the internal olefins cyclohexene (**1a**) and 3-heptene (**1b,c**) (entries 1−3, Table 1). Electron-withdrawing substituents deactivate the C═C double bond toward the electrophilic oxidant,[8] and accordingly, *trans*-2-hexenyl acetate (**1j**) and 2-cyclohexenylacetate (**1l**) required 3 equiv of peracid **2b** (entries 10 and 12, Table 1) to quantitatively convert them into the corresponding epoxides **3**. However, 2 equiv of peracid **2b** sufficed for 3-cyclohexenylmethyl acetate (**1h**) and methyl 2-cyclohexenylcarboxylate (**1i**) (entries 8 and 9, Table 1), since the longer distance between the functional groups in the former and the weaker electron-withdrawing effect of the substituent in the latter render the C═C double bond less deactivated.

The acidic character of the silica surface became evident for highly acid-sensitive epoxides **3**. For instance, styrene (**1m**) failed to give the corresponding epoxide **3m** under our reaction conditions. In this instance, the reaction afforded a complex mixture of products which remained adsorbed on the silica surface. This result was attributed to the acid sensitivity of styrene oxide (**3m**) and the overoxidation of the rearranged products. Substrate conversion was very poor in this case (<10%) due to depletion of peroxidic ligands in the oxidative side processes and the low reactivity of styrene.

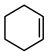
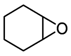
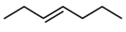
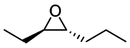
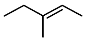
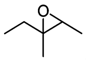
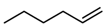
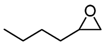
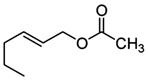
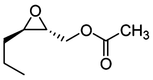
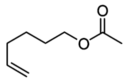
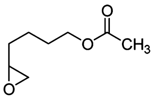
The presence of strong H-bond donor/acceptor substituents in olefin **1** did not interfere with the epoxidation reaction but led to the strong adsorption of the corresponding epoxide **3** on the silica surface. For instance, epoxidation of 2-cyclohexen-1-ol (**1n**) with a 3-fold excess of peracid **2b** led to its quantitative conversion into epoxide **3n** under our experimental conditions (eq 3). The reaction product had to be recovered by either flowing a solution of ethyl acetate in *sc*CO_2 at 250 bar and 40 °C through the solid reagent or thoroughly washing it with dichloromethane once the system was depressurized. The oxygen transfer reaction took place exclusively on the syn diastereoface of the C═C double bond, which is in agreement with the directing effect reported for the hydroxyl groups in the epoxidation of allylic and homoallylic alcohols with organic peracids under homogeneous conditions.[9] Conversely, epoxidation of the substituted cyclic olefins **1h**,**i**,**l** gave 50:50 mixtures of the syn and anti diastereomers (entries 8, 9, and 12, Table 1).



(3)

The reactions required an excess of oxidant **2b** to achieve the complete conversion of substrates **1** (Table 1). This result can be attributed to the short contact time of the substrate with the supported reagent under the flow conditions (ca. 21 min under our reaction conditions). Control experiments carried out in batch mode for longer reaction periods improved the performance of the solid peracid **2b**, leading to good conversions of substrates despite the system's static character (Table 2). These reactions were carried out at 250 bar and 40 °C with an initial 1:1 molar ratio of alkene **1** and peracid **2b** by pressurizing with CO_2 a thermostated reactor containing the solid reagent through a Rheodyne valve loaded with the substrate, allowing the system to stand for 90 min, and then flowing *sc*CO_2 at 250 bar and 40 °C for 2 h to collect the reaction products in a cooled trap. Substrate conversions were lower for terminal olefin **1g** and alkenyl esters **1j**,**k** (entries 4–6, Table 2) than for internal olefins **1a**,**b**,**d** (entries 1–3, Table 2), in agreement with the distinct reactivity of olefins **1** toward electrophilic oxidant **2b**. Mass balances were correct in all cases except for the most reactive olefin **1d** which, under these conditions, led to a mixture of products derived from the acid-catalyzed reactions of epoxide **3d** and to the overoxidation of the rearranged products. The organic material remained adsorbed on the solid reagent and was recovered by thoroughly washing it with methanol. This result indicates that using an excess of anhydrous solid peracid **2b** proves to be a more convenient approach to achieve the quantitative conversion of the less reactive olefins **1** than prolonging the reaction time.

Table 2. Oxidation of Alkenes 1 with [SiO_2]-CH_2CH_2COOOH (2b) in *sc*CO_2 in Batch Mode[a]

Run	Substrate	Product[b]	Conv.[c]
1	 **1a**	 **3a**	83
2	 **1b**	 **3b**	80
3	 **1d**	 **3d**	92[d]
4	 **1g**	 **3g**	45
5	 **1j**	 **3j**	22
6	 **1k**	 **3k**	28

[a]Reactions in *sc*CO_2 at 250 bar, 40 °C, with anhydrous **2b** (1.2 mmol of peracid g^{-1}) and molar ratio alkene **1**:peracid **2b** 1:1 for 90 min. The reaction product was extracted with *sc*CO_2 at a flow rate of 0.11–0.12 mL of *sc*CO_2 min^{-1}. [b]Epoxides **3** were the only products (yield >99%), except where indicated. [c]Determined by GC analysis of the reaction mixtures; mass balance >98% in all cases. [d]Products derived from acid-catalyzed side reactions were isolated from the solid reagent.

Use of anhydrous silica-supported potassium peroxomonosulfate, $KHSO_5$,[5] a much stronger electrophilic oxidant than organic peracids, for the epoxidation of the less reactive olefins **1** did not improve reaction efficiency, as the strongly acidic character of the silica surface, which is covered by the $KHSO_4$ species from the Caroate triple salt used for preparing the reagent and generated in the oxygen transfer reaction, promoted extensive acid-catalyzed side reactions of epoxides **3** and the overoxidation of the rearranged products.

CONCLUSIONS

2-Percarboxyethyl-functionalized silica (**2b**) is a suitable reagent to perform the epoxidation of alkenes **1** in supercritical carbon dioxide at 250 bar and 40 °C under flow conditions. Epoxides **3** undergo neither acid-catalyzed ring opening nor any other side reactions under these conditions, provided that the supported peracid **2b** is anhydrous. The reaction is not suitable for those alkenes **1** carrying strong H-bond donor/acceptor substituents, such as hydroxyl groups. This procedure uses only carbon dioxide as a solvent under mild conditions and simplifies both the isolation of the reaction products and the recovery of the carboxylic acid. Solid reagent **2b** can be easily recycled by a reaction with 30% hydrogen peroxide in an acid medium.

EXPERIMENTAL SECTION

Caution! The experiments described in this paper involve the use of relatively high pressures and require equipment with the appropriate pressure rating.

General Considerations. Reagents and solvents were purified following standard procedures.[10] 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. Hydration of silica-supported peracid **2b** was performed by adding the desired amount of water at room temperature to the anhydrous material and stirring for 6 h in a closed vial. The high-pressure equipment consisted of a 250 mL AISI 316 stainless steel jacketed autoclave, a diaphragm pump (Orlita MHS 30/8) with a maximum theoretical flow of 8.44 L/h of liquid CO_2, a set of high-pressure valves, pressure and temperature probes, and security rupture disks suitably placed to control the flow of CO_2 along the system.

2-Percarboxyethyl-Functionalized Silica (2b). 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 stirred 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 with stirring for 6 h. The solid was filtered and washed with cold doubly distilled 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 per gram of material.

Oxidation of Alkenes with Silica-Supported Peracid 2b in *sc*CO_2. General Procedure. A stainless steel 8 mm i.d. column was packed with 1.35 g of silica-supported peracid **2b** (1.2 mmol g^{-1}, 2 equiv) and tightly closed with two filters placed on either end of the column to prevent any displacement of the solid reagent throughout the experiment. The column outlet was connected to a high-pressure micrometric valve which was connected to a trap cooled with a dry ice bath through a $^1/_8$ in. Teflon tube. The pressure in the trap was equilibrated with a flow of nitrogen. The 250 mL autoclave set at 40 °C was connected to the column inlet by a Rheodyne valve. The autoclave was charged with CO_2 and pressurized to 250 bar. Then both the loop of the Rheodyne valve and the column were placed in a water bath heated to 40 °C, and the system was pressurized by carefully opening the inlet valve. The stroke volume of the pump and the aperture of the high-pressure micrometric outlet valve were regulated to achieve steady continuous-flow conditions at 250 bar. The CO_2 flow at the system outlet was monitored with a bubble flow meter. The Rheodyne valve was loaded with 82 μL (0.8 mmol) of cyclohexene (**1a**), which was then injected into the system once the work regime had been achieved. The system was left to operate for 2 h. The inlet valve was then closed and the system was depressurized. The trap was warmed to room temperature, and the colorless residue was dissolved in deuterated chloroform and analyzed with the aid of GC, GC-MS, ^{1}H, and ^{13}C NMR techniques. The solid reagent recovered from the column was washed four times with 15 mL of dichloromethane in a round-bottomed flask with magnetic stirring. The filtered solution was analyzed by means of GC and then evaporated under vacuum at 0 °C.

Cyclohexene Oxide (3a) [286-20-4]. ^{1}H 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, [$M^{•+}$]).

(E)-3-Heptene Oxide (3c) [56052-95-0]. ^{1}H 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, [$M^{•+}$]).

(Z)-3-Heptene Oxide (3b) [56052-94-9]. ^{1}H 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, [$M^{•+}$]).

(Z)-3-Methylpentene Oxide (3d) [1447-39-8]. ^{1}H 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, [$M^{•+}$]).

exo-Norbornene Oxide (3e) [3146-39-2]. ^{1}H 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, [$M^{•+}$]).

2-Phenylpropene Oxide (3f) [4436-24-2]. ^{1}H 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, [$M^{•+}$]).

1-Hexene Oxide (3g) [592-41-6]. ^{1}H 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, [$M^{•+}$]).

1-Methylcarbonyloxymethyl-3-cyclohexene Oxide (3h) [75228-31-8]. Mixture of isomers 50:50. ^{1}H 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, [$M^{•+}$]); isomer 2, 43 (100), 55 (21), 67 (43), 81 (81), 95 (37), 110 (43), 127 (23), 170 (0, [$M^{•+}$]).

1-Methoxycarbonyl-2-cyclohexene Oxide (3i) [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, $CDCl_3$): major isomer, δ 22.7, 22.8, 27.1, 35.6, 51.6, 51.7, 52.1, 175.8; minor isomer, δ 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, [$M^{•+}$]); minor isomer, 67 (26), 70 (29), 81 (41), 87 (19), 97 (100), 100(21), 113 (7), 128 (6), 141 (1), 156 (0.7, [$M^{•+}$]).

(E)-1-Methylcarbonyloxy-2-hexene Oxide (3j) [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, [$M^{•+}$]).

1-Methylcarbonyloxy-5-hexene Oxide (3k) [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, [$M^{•+}$]).

1-Methylcarbonyloxy-2-cyclohexene Oxide (3l) [84414-68-6]. Mixture of isomers 60:40. ^{1}H 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, $CDCl_3$): major isomer, δ 14.4, 21.1, 23.6, 25.7, 52.5, 53.3, 68.0, 170.1; minor isomer, δ 19.3, 21.1, 22.5, 24.4, 52.8, 54.2, 70.8, 170.8. EM (EI$^+$, 70 eV; m/z (rel abund0): major isomer, 43 (100), 55 (18), 68 (18), 70 (54), 86 (9), 96 (17), 112 (21), 156 (0, [$M^{•+}$]); minor isomer, 43 (100), 55 (14), 67 (18), 70 (61), 86 (5), 96 (19), 112 (24), 156 (0, [$M^{•+}$]).

1-Hydroxy-2-cyclohexene Oxide (3n) [1192-78-5]. ^{1}H 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, [$M^{•+}$]).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving ^{1}H and ^{13}C NMR spectra for 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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