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ORIGINAL PAPER

Functionalization of Oleyl Carbonate by Epoxidation

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Abstract Carbonates (esters of carbonic acid H_2CO_3) are a class of compounds that are of increasing interest in commercial applications due to their physical properties and relatively straightforward synthesis. Herein, oleyl carbonate, an oleochemical-based compound derived from oleyl alcohol, was epoxidized utilizing performic acid generated in situ from formic acid and 50% H_2O_2. The reaction proceeded smoothly and furnished the corresponding oleyl carbonate bisepoxide, (bis[8-(3-octyloxiran-2-yl)octyl] carbonate), in good yields (83–85% isolated yields after purification by silica gel chromatography). The carbonate moiety was found stable to the reaction conditions utilized for epoxidation and the isolated oleyl carbonate bisepoxide was subsequently characterized using Fourier transform infrared spectroscopy, ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR), and liquid chromatography electrospray ionization mass spectrometry. Oleyl carbonate bisepoxide compound may be of potential interest as a plasticizer, monomer, or a substance for further chemical elaboration.

Keywords Oleyl carbonate · Dialkyl carbonate · Epoxidation · Hydrogen peroxide · Performic acid · Nuclear magnetic resonance · Mass spectrometry

Introduction

Renewable feedstocks such as fats, oils and starch, obtained from plant and animal sources, represent important raw materials used as chemical building blocks throughout the chemical industry. The ability to effectively functionalize these materials and extend their potential chemistry and applications will facilitate further development of sustainable chemistry. Oleochemical-based carbonates (ROCOOR) [1–3] represent one such class of compounds of interest that are derived from long-chain alcohols and currently find use as components in lubricants [4], cosmetics [5], and plasticizers [6]. In particular, oleyl carbonate, **1**, can be conveniently prepared in good yields from oleyl alcohol through a variety of methodology [1, 2] such as the carbonate interchange reaction with dimethyl or diethyl carbonate, Scheme 1.

Although simply prepared, studies examining the properties and uses of oleyl carbonate are limited to patent reports [7–12] whereby oleyl carbonate is used in conjunction with a host of other compounds. This literature suggests oleyl carbonate is a useful component in lubricant formulations [7–10], as a component in cosmetic formulations [11], and in paper sizing [12] formulations.

The ability to effectively functionalize oleyl carbonate's unsaturated sites while maintaining the integrity carbonate group is largely unexplored and development of chemistry to accomplish these objectives could help expand its usefulness into other applications. Accordingly, Fabry and Westfachtel [13, 14] have examined the sulfonation of

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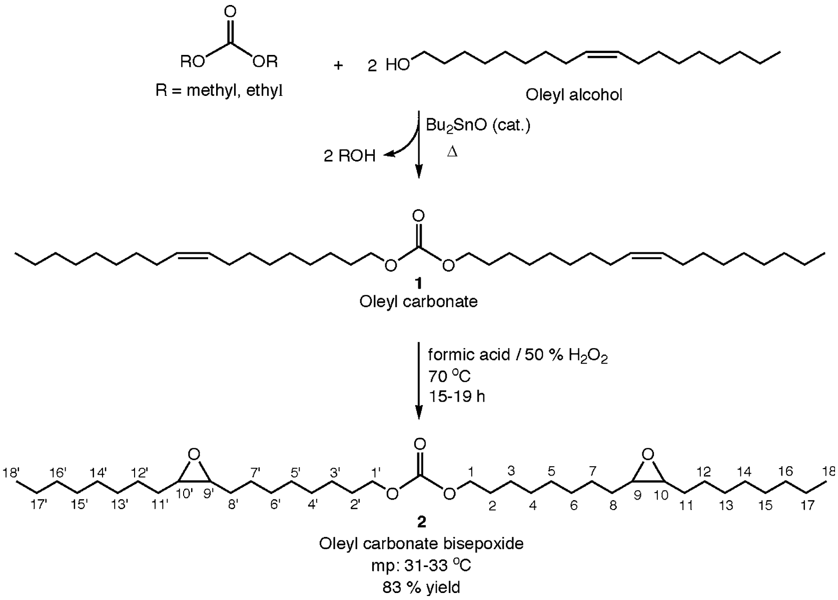
Scheme 1 Overall synthetic Scheme used to prepare **2** from oleyl alcohol via dialkyl carbonate interchange reaction



oleyl carbonate's unsaturated sites utilizing gaseous sulfur trioxide at a temperature between 40 and 45 °C. In this work, the carbonate moiety was utilized as a hydroxyl protecting group for oleyl alcohol and endured the strongly acidic sulfonation reaction conditions. Subsequent hydrolysis of the carbonate group liberated carbon dioxide as a byproduct and simultaneously provided two long-chain hydroxyl alkyl sulfonate molecules that were found to posses surface active properties [13, 14]. Outside of these patent reports, to our knowledge, no other research examining the reaction chemistry surrounding oleyl carbonate has been reported.

The epoxidation of vegetable oils, FA, and FA esters represents an important industrial process that provides materials utilized in a broad range of applications such as plasticizers and stabilizers for halogen-containing polymers such as polyvinyl chloride [15], polyols for polymeric foams and coatings [16, 17], and lubricants [18]. In light of the epoxide group's versatility, the epoxidation of the two unsaturated sites in oleyl carbonate utilizing performic acid, generated in situ from formic acid and 50% H_2O_2, was explored as a means to functionalize oleyl carbonate, provide a new type of compound, and also examine oleyl carbonate's reaction chemistry. Under the reaction conditions utilized, complete epoxidation of oleyl carbonate's two unsaturated sites was accomplished in good yields (80–85% after purification). This unique low melting (31–33 °C) long-chain compound was characterized by ^{1}H- and ^{13}C nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), as well as liquid chromatography–electron spray ionization–mass spectrometry (LC–ESI–MS).

Experimental Procedures

Materials

All chemicals were used without further purification unless otherwise noted. Technical grade (85%) oleyl alcohol was purchased from the Aldrich chemical company (Milwaukee, WI) while higher purity oleyl alcohol was obtained from NuChek Prep (Elysian, MN). Formic acid 99% was obtained from Acros Chemicals (Morris Plains, NJ). Hydrogen peroxide (50% in H_2O by weight) was purchased from the Aldrich Chemical Co. (Milwaukee, WI). Chloroform, ethyl acetate, and methanol were obtained from theFisher Scientific Co. (Fairlawn, NJ).

Oleyl Carbonate (**1**)

Oleyl carbonate was prepared from technical grade (20–23% *trans*-isomer) or higher purity oleyl alcohol (5–8% *trans*-isomer), respectively, following a previously published literature procedure [2]. The relative amount of *trans*-isomer contained in oleyl alcohol was determined by comparing the integration results for the *cis*-(5.32–5.39 ppm) and *trans*-(5.38–5.42 ppm) vinyl hydrogen signals in the NMR spectra [19]. Purified oleyl carbonate, **1**, obtained from reaction of technical grade oleyl alcohol, was found to contain approximately 22–24% *trans*-double bonds (by ^{1}H NMR) while the oleyl carbonate prepared from the higher purity oleyl alcohol contained approximately 8.5% *trans*-double bonds. The relative amounts of *trans*-isomer in these preparations of **1** were determined by comparing integration results for the *cis*-(5.33–5.39 ppm) and *trans*-(5.39–5.42 ppm) vinyl hydrogen signals in the NMR spectra [19].

Melting Points

Melting points were determined on a Fisher Johns melting point apparatus and are uncorrected.

Thin Layer Chromatography (TLC)

Analytical TLC was carried out using 250 µm silica gel 60f254 plates purchased from Alltech Associates Inc. (Deerfield, IL). The eluent was 90:10 chloroform:methanol. Eluted plates were visualized by $KMnO_4$ staining.

Nuclear Magnetic Resonance (NMR)

^{1}H NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 500 spectrometer (Billerica, MA) using a 5 mm broadband inverse Z-gradient probe (500.13 MHz ^{1}H/125.77 MHz ^{13}C) using $CDCl_3$ (Cambridge Isotope Laboratories, Andover, MA) as the solvent in all experiments.

Fourier Transform-Infrared (FTIR)

IR spectra were obtained using a Thermo Nicolet Nexus 470 FT-IR E.S.P. as a film on a diamond anvil.

Liquid Chromatography–Electrospray Ionization–Mass Spectrometry (LC–ESI–MS)

Samples were run on a Finnigan-Thermoquest LCQ LC-MS system (AS3000 autoinjector, P4000 HPLC pump, UV6000 PDA detector, LCQ ion-trap mass spectrometer and a nitrogen generator) (San Jose, CA) all running under the Xcaliber 1.3 software system. The MS was run with the ESI probe in the positive mode. The column was a 3 × 150 mm Inertsil reverse phase C-18, ODS 3, 3-µm column (Metachem, Torrance, CA) with a Metaguard guard column. The solvent system was 20% water 80% methanol with 0.25% acetic acid, at a flow rate of 0.1 mL per min. The source inlet temperature was set at 225 °C and the sheath gas rate was set at 88 arbitrary units with an auxiliary gas flow rate of 12 arbitrary units. The MS was optimized for the detection of the oleyl carbonate epoxide (**2**) by using the autotune feature of the software while infusing a solution of **2** in with the effluent of the column and tuning on an atomic mass unit of 595 $[M + H]^+$. For analysis, the sample was injected into the post column flow. The software package was set to collect mass data between 150 and 1,000 AMUs.

Representative Procedure for the Synthesis of Oleyl Carbonate Bisepoxide (**2**)

In a three-neck round bottom flask equipped with a magnetic stir bar and reflux condenser, a mixture of oleyl carbonate (9.92 g, 17.7 mmol, prepared from 85% technical grade oleyl alcohol that contained *ca*. 24% *trans*-isomer) and 99% formic acid (756 mg, 16.3 mmol) was heated to 40 °C. Hydrogen peroxide (50 wt% in H_2O_2, 21.5 mL, 350.7 mmol) was added dropwise over 10 min to the mixture maintained at 40 °C. After the H_2O_2 addition was complete the reaction mixture was refluxed at 70 °C for 19 h while vigorously stirred. Reaction progress was followed by TLC and when deemed complete, the reaction mixture was cooled and taken up in ethyl acetate (50 mL). The ethyl acetate layer was separated from the aqueous phase and washed with saturated NaCl solution (1 × 20 mL), saturated Na_2CO_3 solution (2 × 20 mL), and saturated NaCl solution (1 × 20 mL). The ethyl acetate was dried ($MgSO_4$), filtered, and concentrated in vacuo on a rotary evaporator. The crude product (9.95 g, 94.9% yield) was then placed under vacuum overnight at 22 °C. Silica gel column chromatography using chloroform:methanol (90:10) as the eluent gave 8.74 g (83.3% yield) of oleyl carbonate bisepoxide, **2**, as a white waxy material after vacuum drying.

Oleyl carbonate bisepoxide, **2**: mp: 31.0–33.0 °C, (mp reported for compound **2** containing approximately 6% *trans*-epoxy isomer)

^{1}H NMR: δ 4.14 (*t*, 4H, J = 6.7 Hz, $-(O{=})C{-}OCH_2-$), 2.92 (*bs*, 4H, *cis*-epoxy H), 2.66 (*bm*, 4H, *trans*-epoxy H), 1.68 (*m*, 4H, $-(O{=})C{-}OCH_2CH_2-$), 1.55–1.25 (*m*, 52H, alkyl chain H), 0.90 (*t*, 6H, J = 6.9 Hz, $-CH_3$). ^{13}C NMR: δ 155.44 (carbonate C=O), 67.99 (C1, C1′), 58.94 (C9, C9′, C10, C10′; *trans*-isomer, minor peak), 58.91 (C9, C9′, C10, C10′; *trans*-isomer, minor peak), 57.23 (C9, C9′, C10, C10′; *cis*-isomer), 57.20 (C9, C9′, C10, C10′; *cis*-isomer), 31.86 (C16, C16′), 29.56, 29.53, 29.45, 29.41, 29.22, 29.13, 28.68 (C2, C2′), 27.84 (C8, C8′, C11, C11′), 27.82 (C8, C8′, C11, C11′), 26.60, 26.59, 25.68, 22.66 (C17, C17′), 14.09 (terminal $-CH_3$). IR (diamond anvil, Nicolet) cm^{-1}: 2955, 2916, 2848, 1743 (C=O), 1466, 1261 (epoxide), 945, 845, 719. LC-ESI-MS (positive ion): *m/z* 635 $[M + Na + H_2O]^+$, 617 $[M + Na]^+$ (base peak), *m/z* 595 $[MH]^+$, *m/z* 329 $[C_{19}H_{37}O_4]^+$, *m/z* 267 $[C_{18}H_{35}O]^+$.

Results and Discussion

We have previously reported the preparation and spectrometric characterization of oleyl carbonate, **1**, using a carbonate interchange reaction between oleyl alcohol and diethyl carbonate in the presence of *n*-dibutyltin catalyst, Scheme 1 [2]. Good yields of oleyl carbonate were obtained after kügelrohr distillation. The epoxidation of oils and their derivatives are commonly performed utilizing performic or peracetic acids, because of their easy availability and low price [15–18]. Performic acid, generated in situ from formic acid and 50% H_2O_2, was used to epoxidize oleyl carbonate as shown in Scheme 1. The epoxidation reaction proceeded relatively slowly, and the oleyl carbonate was typically consumed after 15–19 h when the reaction mixture was refluxed at 70 °C with vigorous stirring. The reaction progress and yields were dependent on stirring efficiency, as poor stirring gave low yields of epoxidized product, presumably, due to the poor physical contact between the oleyl carbonate phase and the aqueous phase containing performic acid oxidant. After reaction, the crude product was typically isolated in crude yields of 95% or better. Purification by silica gel chromatography gave a white waxy solid in isolated yields ranging between 80 and 85%.

The ^{1}H NMR spectra of the starting oleyl carbonate, **1**, that contained approximately 8.5% *trans*-double bonds, and epoxidized product, **2**, are shown in Fig. 1, spectra A and B. Comparison of these spectra clearly shows the near total conversion of double bonds to epoxy rings through the disappearance of oleyl carbonate's vinyl and allylic hydrogen signals located at 5.3–5.4 ppm and 2.0 ppm, respectively (spectrum A), and the appearance of epoxide hydrogens at 2.66 and 2.92 ppm along with a new signal at 1.50 ppm (spectrum B). The signal located at 1.50 ppm corresponds to the C8 and C11 methylene hydrogens adjacent to the epoxide ring (C8′ and C11′ chemical shifts are identical) and were subsequently confirmed through 2D homo- and hetero-nuclear correlation (COSY and HSQC) NMR experiments. The two signals located at 2.66 and 2.92 ppm, attributed to the epoxy ring methine hydrogens (C9, C9′, C10, and C10′) are characteristic of *trans* and *cis* epoxy hydrogens, respectively. Indeed, the *cis* and *trans* epoxy hydrogen assignments for these signals appear eminently reasonable based on ^{1}H NMR chemical shift data reported for long-chain fatty esters such as methyl *cis*-9,10-epoxy stearate (epoxide hydrogens at 2.88 ppm) and methyl *trans*-9,10-epoxy stearate (epoxide hydrogens at 2.63 ppm) which are in good agreement to those observed for **2** [20]. Gunstone has also reported ^{1}H NMR data for the entire series of methyl *cis* and *trans* epoxyoctadecanoates and has noted the ^{1}H NMR chemical shifts of the *cis* epoxy hydrogens fall downfield relative to the *trans* epoxy hydrogens [21].

The amount of *trans*-epoxide present in **2** was determined to be 6% by integration of the *trans* epoxy hydrogen signal (2.66 ppm) relative to the *cis* epoxy hydrogen signal (2.92 ppm). This amount of *trans*-epoxy determined by NMR agrees closely to the amount of *trans*-double bonds (8%) present in the starting oleyl carbonate.

To further substantiate our *cis* and *trans* epoxy hydrogen assignments, oleyl carbonate **1**, enriched in *trans*-double bonds (approximately 24% *trans*-double bonds), was subjected to epoxidation under similar reaction conditions. The

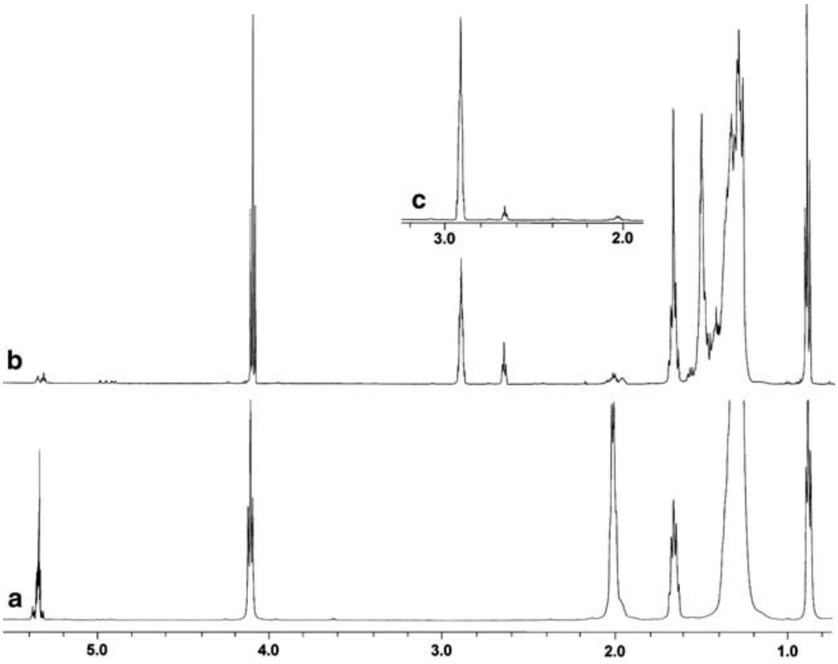


Fig. 1 ^{1}H NMR spectra of: *a* starting oleyl carbonate **1** containing 8.5% *trans*-isomer; *b* oleyl carbonate bisepoxide **2** containing approximately 6% *trans*-epoxide; *c* epoxide region ofoleyl carbonate bisepoxide, **2**, containing approximately 22% *trans*-epoxide

reaction proceeded nicely, and again consumed nearly all the double bonds. Integration of the *trans* epoxy hydrogen signal at 2.66 ppm relative to the *cis* epoxy hydrogens at 2.92 ppm found the *trans* epoxide present in 22%, inset C, Fig. 1. As expected, the amount of *trans*-epoxide present in **2** as determined by NMR agreed closely to the starting amount of *trans* double bonds present in the *trans*-enriched oleyl carbonate used for the epoxidation reaction.

In the ^{13}C-NMR spectrum of **2**, there are clearly marked chemical shift differences, albeit small, between the *cis* and *trans* epoxy carbon atoms. The carbon atoms for the major *cis* epoxide isomer in **2** were readily apparent at 57.23 and 57.20 ppm and were easily seen by distortionless enhancement of polarization transfer (DEPT) NMR experiments. The ^{13}C-NMR signals for the minor *trans*-epoxide isomer, also identified from the DEPT experiments, were located at 58.91 ppm (two signals). The C8, C8′ and C11, C11′ carbon atoms adjacent to the epoxide rings were readily discernible from the 2D NMR experiments and had chemical shifts of 27.84 and 27.82 ppm. These chemical shifts correlated nicely to the similar C8 and C11 carbon atoms in methyl *cis*-9,10-epoxyoctadecanoate located at 27.48 ppm [22]. In contrast, the C8 and C11 carbon atoms for the methyl *trans*-9,10-epoxyoctadecanoate are shifted downfield approximately 4.4–31.89 ppm [22]. In the ^{13}C-NMR spectrum of **2**, small signals, around 31–32 ppm corresponding to the *trans* epoxide isomer were noticeable but were difficult to accurately report due to an interfering signal from the C16, C16′ carbon atoms. Assignments for the terminal C18, C18′ methyls, C17, C17′, C16, C16′, and C2, C2′ carbon atoms, made from DEPT and 2D HMBC and HSQC NMR experiments, were at 14.09, 22.66, 31.86, and 28.68 ppm, respectively. The remaining methylene carbon atoms fell into the typical methylene envelope between 26.68 and 29.56 ppm observed for long-chain fatty esters.

Analysis of epoxidized product **2** by GC and GC-MS was not possible since neither the starting oleyl carbonate nor the epoxidized product were amenable to the GC conditions examined. The positive LC-ESI-MS spectrum of epoxidized carbonate **2** exhibited a small molecular ion $[M + H]^+$ at *m/z* 595 and a large $[M + Na]^+$ sodium adduct ion at *m/z* 617 as the base peak. A small ion at *m/z* 635 due to addition of H_2O to the sodium adduct was also observed. Another small fragment ion at *m/z* 329 was also observed and likely formed by protonation of the carbonate moiety followed by hydrogen rearrangement and bond cleavage to give a $[C_{19}H_{37}O_4]^+$ ion. Cleavage of the bond between the carbonate oxygen and C1 carbon atom gave a small fragment ion at *m/z* 267 corresponding to the $C_{18}H_{35}O$ fragment.

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