Preparation and evaluation of a series of α-hydroxy ethers from 9,10-epoxystearates*

Several novel α-hydroxy ethers were prepared by treatment of isobutyl 9,10-epoxystearate with a number of aliphatic alcohols in the presence of acid catalyst in good overall yield from oleic acid. The low-temperature behavior of each material was analyzed through cloud point (CP) and pour point (PP) determination. The most desirable α-hydroxy ether prepared in this study was isobutyl 9(10)-(2-ethylhexoxy)-10(9)-hydroxystearate. Therefore, additional α-hydroxy-2-ethylhexyl ethers were produced from alkyl 9,10-epoxystearates (alkyl: butyl, hexyl, 2-methylpentyl, 2-ethylbutyl, 2-ethylhexyl) to explore the effect of ester variability on CP and PP of the optimized 2-ethylhexyl ether moiety. The most bulky ester group, 2-ethylhexyl, exhibited the most favorable low-temperature performance, which in the case of 2-ethylhexyl 9(10)-(2-ethylhexoxy)-10(9)-hydroxystearate yielded a CP of -26°C and a PP of -29°C. An improved synthesis of 2-ethylhexyl 9(10)-(2-ethylhexoxy)-10(9)-hydroxystearate was then developed from oleic acid. Lastly, in an effort to optimize yield, sulfuric acid at 10 mol-% was found to be the most effective acid catalyst in the conversion of epoxides to α-hydroxy ethers.

Keywords: Biodiesel, cloud point, epoxidation, α-hydroxy ethers, pour point.

1 Introduction

Vegetable oils and derivatives thereof are used for a variety of industrial non-food applications, which include emulsifiers, lubricants, plasticizers, surfactants, plastics, solvents, and fuels. Lipid-based materials are attractive alternatives to petroleum-derived products because they enjoy enhanced biodegradability, lower toxicity, and they originate from renewable oilseed sources [1]. Biodiesel (BD), defined as the monoalkyl esters of fatty acids derived from vegetable oils or animal fats, is an attractive alternative to petrodiesel (PD) for combustion in compression-ignition (diesel) engines. BD has a number of important advantages over PD, which include reduction of most exhaust emissions, improved lubricity, higher flash point, improved biodegradability, and reduced toxicity [2–5]. Furthermore, a number of BD fuel properties are comparable to PD, such as viscosity, gross heat of combustion and cetane number [2–3]. However, oxidative stability, nitrogen oxides (NOx) emissions, and cold-weather operability are areas where BD is inferior to PD [5–7]. For instance, soybean methyl esters (SME) have a cloud point (CP) of -2°C, which is in stark contrast to no. 2 diesel fuel (-17°C) [8]. Numerous approaches for improving the cold-weather characteristics of BD fuel have been investigated, such as blending with PD, transesterification with long- or branched-chain alcohols, crystallization fractionation, and treatment with commercial PD cold-flow improver (CFI) additives [9]. However, CFI additives designed for PD are rarely effective when used in BD [10–12]; therefore, an important area of current research is the development of novel CFI additives for use in BD fuel. Relevant to the current study is the synthesis and evaluation of potential CFI additives for BD derived from renewable, lipid-based starting materials [13].

Disruption of the arrangement of molecules into an orderly pattern has the effect of lowering the temperature at which crystallization occurs. Such disruptive forces can be introduced synthetically through structural modification. For instance, the m.p. of methyl stearate (MS) is 39°C [14], yet substitution to yield the isobutyl ester (m.p. 23°C) has a significant affect on the crystalline behavior of the substance (Tab. 1). When applied to BD fuel, the same trend is observed, as can be seen by comparison of SME (CP -2°C) and soybean isopropyl esters (SPE, CP -3°C).
The current work describes the synthesis of a series of novel α-hydroxy ethers from 9,10-epoxystearates (Figs. 1, 2) that utilize both head group manipulation and branching strategies to impart favorable low-temperature behavior on lipid-based materials. The products were then evaluated for cold-flow performance through determination of both CP and PP. Furthermore, the effects of mineral acid type, amount, and reaction temperature were examined and optimized for the conversion of oxiranes to α-hydroxy ethers.

2 Materials and methods

2.1 Materials

Formic acid (88%) was obtained from Fisher Scientific (Pittsburgh, PA, USA) and oleic acid (99%) from Nu-Chek Prep, Inc. (Elysian, MN, USA). All other chemicals and reagents were obtained from Aldrich Chemical (Milwaukee, WI, USA). All materials were used without further purification. All organic extracts were dried using anhydrous magnesium sulfate.

2.2 Synthesis

2.2.1 Esterification of oleic acid

To a stirred solution of oleic acid (99%, 1.0 g, 10.0 g, 35.4 mmol) in the desired alcohol (15.0 mL) was added formic acid (88%, 5.0 mL, 117 mmol) (sat. aq., 2 x 5 mL) and brine (2 x 5 mL) (2 x 5 mL). The reaction proceeded at rt with vigorous stirring (900 rpm) until GC-MS analysis indicated conversion of 2-6 (14-16 h). After removal of the lower aqueous phase, hexanes (20 mL) were added to the upper oily phase, which was washed with NaHCO₃ (sat. aq., 2 x 5 mL) and brine (2 x 5 mL). The organic phase was dried, filtered, concentrated in vacuo, and placed for 6 h under high vacuum to afford the alkyl oleate (2-6) as a clear oil (97+ % typical yield). The esterifications employing Cs+ alcohols (2-methylpentanol, 2-ethylbutanol, 2-ethylhexanol) were further dried by Krugelrohr (Buchi Model B-585, Flawil, Switzerland) distillation at 100-120 °C and 0.1-0.5 mmHg to remove excess alcohol. No further purification was performed. 1H-NMR (500 MHz, CDCl₃): δ 5.4 (2H, -CH=CH-), 2.3 (2H, -CH₂CO₂R), 1.6 (2H, -CH₂CH₂CO₂R), 0.9 (3H, -CH₃); 13C-NMR (126 MHz, CDCl₃): δ 174 (R, -CO₂R), 130 (R, -CH=CH-), 34 (CH₂CH₂CH=CH₂), 14 (R, -CH₃). The other signals in the 1H- and 13C-NMR spectra vary with the different ester head groups. FT-IR (neat): ~2893 and ~2853 cm⁻¹ (sharp CH₂ stretches), ~1733 (sharp carbonyl stretch), ~1466 (CH₂ bending vibration), ~1374 (CH₃ symmetrical bending vibration), ~1249, ~1179, and ~1108 (ester C-O stretch).

2.2.2 Epoxidation of alkyl oleates

To a stirred solution of alkyl oleate (2-6, 10.0 g) and formic acid (88%, 5.0 mL, 117 mmol) at 4 °C (ice bath) was added slowly H₂O₂ (30% in H₂O, 8.0 mL, 78 mmol). The reaction proceeded at rt with vigorous stirring (900 rpm) until GC-MS analysis indicated consumption of 2-6 (14-16 h). After removal of the lower aqueous phase, hexanes (20 mL) were added to the upper oily phase, which was washed with NaHCO₃ (sat. aq., 2 x 5 mL) and brine (2 x 5 mL) (2 x 5 mL), dried, filtered, concentrated in vacuo, and placed for 6 h under high vacuum to provide alkyl 9,10-epoxystearate (7-12) as a clear oil (95+ % overall yield, typically). GC-MS analysis generally indicates the presence of <5% alkyl 9,10-dihydroxystearate. No further purification was performed. 1H-NMR (500 MHz, CDCl₃): δ 2.9 (2H, -CH(O)CH-), 2.3 (2H, -CH₂CO₂R), 1.6 (2H, -CH₂CH₂CO₂R), 1.5 (4H, -CH₂CH(O)CH₂), 1.3 (2OH, -CH₂), 0.9 (3H, -CH₃); 13C-NMR (126 MHz, CDCl₃): δ 174 (R, -CO₂R), 35 (R, -CH₂CO₂R), 31 (R, -CH(O)CH-), 14 (R, -CH₃). The other signals in the 1H- and 13C-NMR spectra vary with the different ester head groups. FT-IR (neat): ~2923 and ~2853 cm⁻¹ (sharp CH₂ stretches), ~1733 (sharp carbonyl stretch), ~1466 (CH₂ bending vibration), ~1374 (CH₃ symmetrical bending vibration), ~1249, ~1179, and ~1108 (ester C-O stretch).

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2.2.4 \(\alpha\)-Hydroxy ether formation from alkyl 9,10-epoxystearates

To a stirred solution of 1.0 M solution of alkyl 9,10-epoxystearate (7-11, 1.0 g) in the appropriate alcohol was added \(\text{H}_2\text{SO}_4\) (conc., 10.0 mol-%) and stirring continued at rt until GC-MS analysis indicated consumption of 7-11 (24-240 h). Once the reaction was complete, hexanes (5 mL) were added and the solution was washed with \(\text{NaHC}O_3\) (sat. aq., 1 x 0.5 mL) and brine (2 x 1 mL), dried, filtered, concentrated in vacuo, and placed for 6 h under high vacuum to yield \(\alpha\)-hydroxy ethers 14-25. The reactions employing \(\text{C}_6\text{H}_4\) alcohols were then further dried by Krugelrohr distillation at 100-120°C and 0.1-0.5 mmHg. \(^1\text{H}\)-NMR (500 MHz, CDCl\(_3\)): ~2.7 (1 H, -OH), ~3.3 (1 H, -CH(OH)-), ~3.1 (1 H, -CH(OR')-), ~2.3 (2 H, -CH\(_2\text{CO}_2\)R), ~1.6 (2 H, -CH\(_2\text{CO}_2\)R), ~1.5 (2 H, -CH\(_2\text{CH}_2\)CO\(_2\)R), ~1.3 (2 H, -CH\(_2\text{CH}_2\)CO\(_2\)R), ~0.9 (3 H, -CH\(_3\)). The other signals in the \(^1\text{H}\) and \(^13\text{C}\)-NMR spectra vary with the different ester head groups. FT-IR (neat): 3500 cm\(^{-1}\) (OH stretch) indicative of over-reaction to form a 9,10-dihydroxy byproduct in small (<5%) amount. GC-MS (EI): refer to Tab. 2 for RT of 7-12; 7 m/z 356 [M+H]; 8 m/z 356 [M+H]; 9 m/z 384 [M+H]; 10 m/z 384 [M+H]; 11 m/z 412 [M+H]; 12 m/z 342 [M+H].

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Tab. 2. Percentage yield and retention time (RT) for epoxidation reaction, and CP and PP of alkyl 9,10-epoxystearates.

<table>
<thead>
<tr>
<th>Ester head group</th>
<th>Yield [%]</th>
<th>RT [min]</th>
<th>CP [°C]</th>
<th>PP [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutyl, 7</td>
<td>82</td>
<td>11.13</td>
<td>-9</td>
<td>-10</td>
</tr>
<tr>
<td>Butyl, 8</td>
<td>85</td>
<td>11.50</td>
<td>-9</td>
<td>-10</td>
</tr>
<tr>
<td>2-MP, 9</td>
<td>83</td>
<td>12.47</td>
<td>-6</td>
<td>-13</td>
</tr>
<tr>
<td>2-EB, 10</td>
<td>90</td>
<td>12.53</td>
<td>-9</td>
<td>-12</td>
</tr>
<tr>
<td>2-EH, 11</td>
<td>93</td>
<td>13.59</td>
<td>-3</td>
<td>-13</td>
</tr>
<tr>
<td>Isopropyl, 12</td>
<td>84</td>
<td>10.12</td>
<td>-7</td>
<td>-8</td>
</tr>
</tbody>
</table>

Reactions monitored by GC-MS at 15 ºC until complete.

\[2-EH = 2\text{-ethylhexyl}; \ 2-EB = 2\text{-ethylbutyl}; \ 2-MP = 2\text{-methylpentyl}.

\[\sigma \pm 1 \, ^\circ \text{C}.

From [13].

2.2.5 \(\alpha\)-Hydroxy etherification and esterification of 9,10-epoxystearic acid

To a stirred suspension of 9,10-epoxystearic acid (13, 1.0 g, 3.35 mmol) in the appropriate alcohol (3.35 mL) was added \(\text{H}_2\text{SO}_4\) (conc., 10 mol-%). The suspension was heated with stirring at 60 ºC until GC-MS analysis indicated consumption of 13 (24 h). Upon heating, 13 dissolved. The reaction was processed and characterized as described for 14–25 to provide \(\alpha\)-hydroxy ethers 17 and 26.

2.3 Analysis

2.3.1 NMR

\(^1\text{H}-\text{and} \quad ^{13}\text{C}-\text{NMR spectra were recorded using a Bruker AV-500 spectrometer (Rheinstetten, Germany) operating at a frequency of 500.13 and 125.77 MHz, respectively, using a 5-mm broadband inverse Z-gradient probe in CDCl}_3\) (Cambridge Isotope Laboratories, Andover, MA, USA) as solvent. Each spectrum was Fourier-transformed, phase-corrected and integrated using MestRe-C 2.3a (Magnetic Resonance Companion, Santiago de Compostela, Spain) software.

Tab. 3. Reacton time, percentage yield, and retention time (RT) for ring-opening step, and CP and PP of \(\alpha\)-hydroxy ethers derived from alkyl 9,10-epoxystearates.

<table>
<thead>
<tr>
<th>Ester head group</th>
<th>Ether</th>
<th>rxn temp</th>
<th>rxn time [h]</th>
<th>RT [min]</th>
<th>Yield [%]</th>
<th>CP [°C]</th>
<th>PP [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutyl, 14</td>
<td>Ethyl</td>
<td>rt</td>
<td>24</td>
<td>11.99</td>
<td>77</td>
<td>-9</td>
<td>-14</td>
</tr>
<tr>
<td>Isobutyl, 15</td>
<td>Propyl</td>
<td>rt</td>
<td>48</td>
<td>12.46</td>
<td>86</td>
<td>-11</td>
<td>-14</td>
</tr>
<tr>
<td>Isobutyl, 16</td>
<td>Butyl</td>
<td>rt</td>
<td>72</td>
<td>13.06</td>
<td>82</td>
<td>-16</td>
<td>-20</td>
</tr>
<tr>
<td>Isobutyl, 17</td>
<td>Isobutyl</td>
<td>rt</td>
<td>96</td>
<td>12.61</td>
<td>86</td>
<td>-17</td>
<td>-21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60 ºC</td>
<td>24</td>
<td>87</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Isobutyl, 18</td>
<td>2-ME</td>
<td>rt</td>
<td>72</td>
<td>13.60</td>
<td>78</td>
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<td>-15</td>
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<tr>
<td>Isobutyl, 19</td>
<td>Hexyl</td>
<td>rt</td>
<td>120</td>
<td>14.20</td>
<td>80</td>
<td>-17</td>
<td>-22</td>
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<tr>
<td>Isobutyl, 20</td>
<td>Octyl</td>
<td>rt</td>
<td>240</td>
<td>15.58</td>
<td>82</td>
<td>-19</td>
<td>-22</td>
</tr>
<tr>
<td>Isobutyl, 21</td>
<td>Decyl</td>
<td>rt</td>
<td>264</td>
<td>17.43</td>
<td>85</td>
<td>-20</td>
<td>-22</td>
</tr>
<tr>
<td>Isobutyl, 22</td>
<td>2-EH</td>
<td>rt</td>
<td>168</td>
<td>14.73</td>
<td>87</td>
<td>-20</td>
<td>-23</td>
</tr>
<tr>
<td>Butyl, 23</td>
<td>2-EH</td>
<td>rt</td>
<td>144</td>
<td>15.10</td>
<td>96</td>
<td>-17</td>
<td>-21</td>
</tr>
<tr>
<td>2-EB, 24</td>
<td>2-EH</td>
<td>rt</td>
<td>132</td>
<td>16.35</td>
<td>76</td>
<td>-21</td>
<td>-24</td>
</tr>
<tr>
<td>2-MP, 25</td>
<td>2-EH</td>
<td>rt</td>
<td>136</td>
<td>16.18</td>
<td>78</td>
<td>-20</td>
<td>-25</td>
</tr>
<tr>
<td>2-EH, 26</td>
<td>2-EH</td>
<td>60 ºC</td>
<td>24</td>
<td>17.98</td>
<td>84</td>
<td>-26</td>
<td>-29</td>
</tr>
<tr>
<td>Isopropyl, 27</td>
<td>2-EH</td>
<td>rt</td>
<td>168</td>
<td>13.86</td>
<td>85</td>
<td>-23</td>
<td>-24</td>
</tr>
</tbody>
</table>

Reactions monitored by GC-MS until complete.

\[2-EB = 2\text{-ethylbutyl}; \ 2-EH = 2\text{-ethylhexyl}; \ 2-ME = 2\text{-methoxyethyl}; \ 2-MP = 2\text{-methylpentyl}.

\[\sigma \pm 1 \, ^\circ \text{C}.

From [13].
2.3.2 FT-IR

FT-IR spectra were recorded on a Thermo Nicolet Nexus 470 FTIR system (Madison, WI, USA) with a Smart ARK accessory containing a 45°ZnSe trough in a scanning range of 650-4000 cm\(^{-1}\) for 32 scans at a spectral resolution of 4 cm\(^{-1}\).

2.3.3 GC-MS

Reactions were monitored by GC-MS every 8 or 24 h using a Hewlett Packard (Loveland, CO, USA) 5870 series II GC system equipped with a 6890 series injector and a 5970 series MSD in electron impact (EI) mode. A Supelco SPB-35 (30 m × 0.25 mm) column was used with a helium flow rate of 0.9 mL/min. The temperature program started at 150 °C and increased to 290 °C at 10 °C/min, which was followed by a hold time of 10 min. The inlet and detector temperatures were set to 250 and 280 °C, respectively. The injection volume was 1 µL with a split ratio of 70 : 1. HP-MS ChemStation software was used for data collection and processing.

2.3.4 Low-temperature performance

CP and PP determinations were made in agreement with ASTM D5773 [17] and ASTM D5949 [18] using a Phase Technology Analyzer model PSA-70S (Richmond, B.C., Canada). Each sample was run in triplicate and an average value is reported (Tabs. 2, 3). CP and PP are rounded to the nearest whole degree (°C). For a greater degree of accuracy, PP measurements were done with a resolution of 1 °C instead of the specified 3 °C increment.

3 Results and discussion

3.1 Synthesis

After the straightforward Fischer esterification [19] of oleic acid (1) to provide isobutyl oleate (2), a modified epoxidation protocol [13, 20], originally developed by Swern [21], was employed to provide isobutyl 9,10-epoxy-10(9)-hydroxystearate (7, Fig. 1, Tab. 2). The reaction was followed by GC-MS and stopped when >95% of 2 was consumed (14-15 h). Further analysis by GC-MS of the final product indicated the presence of a small amount (<5%) of isobutyl 9,10-dihydroxystearate, demonstrating the importance of monitoring the epoxidation closely to prevent unwanted over-oxidation. Following a protocol set forth by Aggarwal et al. [22] and Gast et al. [23], ring opening of the oxirane moiety to afford a series of α-hydroxy ethers (Fig. 1) was accomplished by treatment of 1.0 M 7 with H\(_2\)SO\(_4\) catalyst in the desired aliphatic alcohol. The reactions were monitored by GC-MS until 7 was consumed to afford α-hydroxy ethers 14–22 (Tab. 3) in good to excellent yield (77–96%). No effort to distinguish the regiochemistry (isobutyl 9-alkoxy-10-hydroxystearate versus the equally likely isobutyl 10-alkoxy-9-hydroxystearate regiosomer) or the stereochemistry (R or S at C9 and C10) of the α-hydroxy ethers obtained in this study (14–26) was made, due to the laborious chromatography required and the economics involved at potentially larger commercial scales. If such adducts are to be eventually adopted as commercial CFI additives for BD fuel, then production costs relating to synthesis and purification are of paramount importance. Therefore, α-hydroxy ethers 14–26 were evaluated for low-temperature behavior after initial purification as described in Section 2.2.4 as mixtures of regio- and stereoisomers.

Additional 2-ethylhexoxy ethers with different head groups were desired for low-temperature evaluation because isobutyl 9(10)-(2-ethylhexoxy)-10(9)-hydroxystearate (22) provided the lowest CP (−20°C; Tab. 3) and PP (−23°C) of all of the α-hydroxy ethers obtained in this study (14–26). Therefore, analogous to the method described previously, 1 underwent Fisher esterification with 1-butanol, 2-ethylbutanol, 2-methylpentanol, and 2-ethylhexanol to provide the corresponding alkyl oleates (3–6), followed by epoxidation to give oxiranes (8–11; Tab. 2). Each of the epoxides (8–11) was treated with H\(_2\)SO\(_4\) (cat.) and 2-ethylhexanol as described previously to afford alkyl 9(10)-(2-ethylhexoxy)-10(9)-hydroxystearates (23–26), which were evaluated for CP and PP.

The derivative that possessed the most favorable cold-flow characteristics (Section 3.2) was 2-ethylhexyl 9(10)-(2-ethylhexoxy)-10(9)-hydroxystearate (26); therefore, a more facile route was desired in which 26 could be produced in a shorter synthetic sequence. Because the ester and ether moieties are both derived from 2-ethylhexanol in 26, an analogous route was borrowed and modified (Section 3.3) from Gast et al. [23] in which 9,10-epoxy-10(9)-hydroxystearic acid (13) was treated with 2-ethylhexanol and H\(_2\)SO\(_4\) catalyst at 60 °C for 24 h to afford 26 in two steps from 1 instead of the previously described three (Fig. 2). Additionally, 17 may also be produced from the shorter sequence as both the ester and ether moieties are identical (isobutyl).

A number of observations were made regarding the reactivity of alcohols with 7. Firstly, the use of methanol resulted in transesterification to provide methyl 9(10)-methoxy-10(9)-hydroxystearate at rt and none of the desired isobutyl ester. Modification of the reaction conditions, such as lower reaction temperatures and
3.2 Low-temperature performance

The \(\alpha\)-hydroxy ethers (14–26) described above were screened for low-temperature behavior through determination of both CP and PP. Isobutyl 9,10-epoxystearate (7), the precursor for the synthesis of 14–22, exhibited a CP of \(-9^\circ C\) and a PP of \(-10^\circ C\), which is an improvement over SME but not as good as SPE (Tab. 2). The remaining epoxides, 8–12, displayed similar low-temperature behavior. The \(C_2\) and \(C_3\) ethers, ethyl (14) and propyl (15), had similar cold-flow performance to 7, whereas the remaining ethers of longer chain length (16–26) were far superior to epoxides 7–12. As expected, as the chain length of the alcohol increased, a corresponding improvement in CP and PP was observed, which may be due to the greater ability of the longer-chain ethers to more effectively disrupt macrocrystalline formation at reduced temperatures. A positive effect on the low-temperature performance of the resultant \(\alpha\)-hydroxy ether was observed when a branched alcohol was used. For instance, butyl ether 16 has a CP and PP of \(-16^\circ C\) and \(-20^\circ C\), respectively, whereas isobutyl ether 17 has slightly improved values of \(-17^\circ C\) and \(-21^\circ C\), respectively. A similar trend was also observed for the \(C_3\) ethers [octyl (20) and 2-ethylhexyl (22)]. Furthermore, a dramatic improvement in CP and PP of \(\alpha\)-hydroxy ethers is observed when the ether moiety contains four or more carbons (16, 17, 19–26) versus ethers with three or fewer carbons (14, 15, 18). The material that exhibited the best low-temperature behavior in this study, 2-ethylhexyl 9(10)-(2-ethylhexoxy)-10(9)-hydroxystearate (26), was found to have a CP and PP of \(-26^\circ C\) and \(-29^\circ C\), respectively (Tab. 3). Isopropyl 9(10)-(2-ethylhexoxy)10(9)-hydroxystearate (27) was prepared previously [13] and does not perform as well as 26, as can be seen from Tab. 3.

3.3 Evaluation of acid type, concentration, and temperature on formation of 26

A previously reported [23] synthesis of \(\alpha\)-hydroxy ethers using \(C_1–C_3\) alcohols (R = R', Fig. 2) from 13 utilized \(H_2SO_4\) at 2.15 mol-% and a reaction temperature of 100 °C. Repetition of this protocol in the current study using 2-ethylhexanol failed to yield 26 in acceptable yield. Therefore, a series of reactions was performed on the conversion of 13 to 26 (Fig. 2) in which we set out to optimize the yield of 26 by examination of the acid type, amount, and temperature of the reaction.

3.3.1 Acid type

Four common acids, \(H_2SO_4\), \(H_3PO_4\), HCl, and \(para\)-toluenesulfonic acid (pTsOH), were investigated. Firstly, pTsOH was found to be completely ineffective, failing to yield 26 regardless of amount, temperature, or reaction time. Secondly, the mineral acids proved more effective as the molarity of the acid increased. Therefore, \(H_2SO_4\) (18 M) was most effective in providing 26, with \(H_3PO_4\) (14.8 M) and especially HCl (12 M) being less productive (Fig. 3).

3.3.2 Amount of acid

Two catalytic amounts of the mineral acids were investigated: 2 mol-% to approximate the conditions used in [23] and a more traditional 10 mol-%. As expected, the higher amount of acid resulted in shorter reaction times, regardless of the acid chosen (Fig. 3). Hence, 10 mol-% is recommended. Interestingly, \(H_2SO_4\) at 2 mol-% is far more effective than either \(H_3PO_4\) or HCl at 10 mol-%. HCl is almost completely ineffective at either 2 or 10 mol-%; therefore, it is clearly an unacceptable choice for the conversion of 13 to 26. When employing \(H_2SO_4\) at 10 mol-%, the conversion is nearly complete after 24 h. If 2 mol-% \(H_2SO_4\) is used, then the time to reaction completion increases to 50 h. Interestingly treatment of 13 with \(>20\) mol-% \(H_2SO_4\) yields a large percentage (>50%) of unwanted by-products before 13 is >90% consumed, such as dehydrated or sulfonated species, and hydrolysis adducts.

3.3.3 Reaction temperature

Three temperatures were selected for investigation: rt, 60 °C, and 100 °C. As expected, the rate of reaction increased significantly with increasing temperature. In fact, reactions performed at rt, regardless of acid type and amount, were extremely sluggish or completely ineffective. Both of the elevated temperatures in the case of
H₂SO₄ were adequate to yield 26. The middle temperature, 60 °C, afforded 26 in 24–28 h using 10 mol-% H₂SO₄. Increasing the reaction temperature to 100 °C with otherwise similar conditions greatly reduced the time to completion to 3–4 h; however, the purity of the final product was compromised by unwanted by-product formation. Therefore, a temperature of 60 °C is recommended using 10 mol-% H₂SO₄ (Fig. 3). Lastly, neither H₃PO₄ nor HCl at either 2 or 10 mol-% were as effective as 2 mol-% H₂SO₄ at any temperature in providing 26.

4 Conclusions

The 2-ethylhexyl ethers (22-26) exhibited the most favorable cold-flow characteristics, as determined by CP and PP. Of the 2-ethylhexyl ethers, 2-ethylhexyl 9(10)-(2-ethylhexoxy)-10(9)-hydroxystearate (26) yielded the best performance, with CP and PP of ~26 °C and ~29 °C, respectively. The synthesis of 26 (and 17) was shortened in comparison to the other α-hydroxy ethers to take advantage of the identical nature of the ester and ether moieties. Furthermore, in the conversion of 13 to 26 (or 17) 10 mol-% H₂SO₄ was the most effective catalyst at a temperature of 60 °C.

Future work may entail evaluating 26 and other promising α-hydroxy ethers at additive levels in SME. Additional physical property examination (such as thermal and oxidative stability, kinematic viscosity, lubricity, surfactant behavior, etc.) of selected α-hydroxy ethers may provide interesting insights into the utility of these lipid-based derivatives. Lastly, application of the synthetic sequence described herein to epoxidized soybean oil to afford α-hydroxy ethers, and subsequent physical property evaluation, may yield potentially useful value-added products.

Fig. 3. Progression of α-hydroxy ether formation using different acid catalysts at 2 and 10 mol-% at 60 °C in 1.0 M 9,10-epoxy-stearic acid in 2-ethylhexanol.

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References


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