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ORIGINAL PAPER

1,2-Isopropylidene Glycerol Carbonate: Preparation, Characterization, and Hydrolysis

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Abstract Utilization of excess glycerol supplies derived from the burgeoning biodiesel industry is of major importance to the oleochemical industry as the economic viability of the biodiesel and oleochemical industries are closely linked to glycerol prices. Carbonates based on glycerol, such as glycerol carbonate, are gaining prominence due their simple preparation, interesting properties and chemistry. Herein, the synthesis, physical properties, and chemistry of an interesting glycerol-based carbonate (**4**, bis[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl] carbonate; 1,2-isopropylidene glycerol carbonate or solketal carbonate) is reported. Carbonate interchange reaction between solketal (isopropylidene glycerol) and diethyl carbonate in the presence of sodium methoxide catalyst gave solketal carbonate, **4**, in 65–70% isolated yields. Carbonate **4** was characterized using Fourier transform infrared spectroscopy (FTIR), ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR), and gas chromatography–mass spectrometry (GC/MS). The kinematic viscosity at 40 °C, refractive index, and melting point of **4** were determined to be 26.7 mm^2/s, n_D^{20} 1.4460, and below −50 °C, respectively. Using a high frequency reciprocating rig (HFRR) testing apparatus neat **4** was shown to have lubricity properties similar to fatty acid esters. Hydrolysis of the isopropylidene groups converted carbonate **4** into polyol **6**, bis(2,3-dihydroxypropyl) carbonate in good yields (84%). Carbonate polyol **6** was characterized by ^{1}H and ^{13}C NMR and represents a potentially novel polyol component that may be useful in the syntheses of interesting carbonate containing esters and polymers.

Keywords Dialkyl carbonates · Glycerol · Solketal · 1,2-Isopropylidene glycerol · Hydrolysis · Glycerin · 1,2-Isopropylidene carbonate · Carbonate interchange reaction · Nuclear magnetic resonance · Mass spectrometry

Introduction

Growing interest in the use of renewable feedstocks derived from vegetable and animal sources has led to renewed interest in the development of bio-based materials. Much of this effort has focused upon the use and chemical derivatization of primary oleochemicals such as fatty acids, fatty acid esters, and mono- and diglycerides without much regard to secondary byproducts such as glycerol [1]. Glycerin forms the backbone of all triacylglycerols which are the principal constituents of all fats and oils. It is present in approximately 10 wt% in oils and fats and is a value-added byproduct produced from oil and fat saponification and transesterification reactions performed during oleochemical and biodiesel manufacturing processes [2, 3].

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Since the late 1990s, increased global production of biodiesel has created an abundance of crude glycerin that has significantly impacted the glycerin market resulting in a decline in glycerin pricing [2–4]. Because the economic viability of the biodiesel and oleochemical industries are closely linked to glycerol supply and prices, the deterioration of glycerol pricing unfavorably impacts on these industries. Although, significant recent research has focused on using glycerol as a platform chemical to replace mainstream petroleum derived chemicals [2, 5], further development of chemistry and uses for existing commercially available glycerol derived compounds is also a sensible approach. For example, the glycerol derivative, glycerol carbonate, can be converted into glycidol and nicely demonstrates this approach [2, 5–7].

Isopropylidene glycerol **1**, also known as solketal, is a commercially available glycerol derivative prepared by reaction between glycerol and acetone to obtain a protected form of glycerol, whereby, an isopropylene group is covalently bonded to two vicinal hydroxyl groups. Although well known, it appears to be underutilized, finding limited use as a solvent, plasticizer, and a starting material for the preparation of specialty monoglycerides and chemicals [8, 9].

However, carbonates (esters of carbonic acid, RO-COOR) are generally considered safe non-corrosive molecules that are readily prepared [10, 11] and of interest for lubricant [12, 13], cosmetic [14, 15], plasticizer [16], and fuel [17] applications. Although a sizeable body of patent literature and commercial applications exist for carbonates, to our knowledge, the only glycerol derived carbonate compounds reported thus far are glycerol carbonate [6] and polyglycerol compounds that have been subsequently functionalized to contain cyclic carbonate groups [18].

In the present work, solketal carbonate, **4**, (bis[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl]carbonate) was prepared in 65–70% isolated yields (after distillation) through a carbonate interchange reaction between readily available glycerol-derived solketal, **1**, and diethyl carbonate using sodium methoxide as catalyst, Scheme 1. Carbonate **4** was characterized using Fourier transform-infrared (FTIR), gas chromatography (GC), ^{1}H and ^{13}C nuclear magnetic resonance (NMR), and gas chromatography/mass spectrometry (GC/MS) and some of its physicochemical properties such as lubricity were determined. The removal of carbonate **4**'s isopropylidene groups to obtain the corresponding polyol **6**, bis(2,3-dihydroxypropyl) carbonate was also examined. Polyol carbonate **6** represents a polyol component that may be useful in the syntheses of interesting carbonate based polymers.

Experimental Procedures

Materials

Chemical reagents were purchased from Aldrich Chemical Co. (Milwaukee, WI). Grade 22 silica gel (60–200 mesh) was used for chromatography. Amberlite IR-120(plus) strongly acidic ion exchange resin was washed in methanol until the methanol phase was colorless. The resin was then dried in a vacuum overnight before use. Methylene chloride, methanol, acetone, and hexane, were obtained from Fisher Scientific Co. (Fairlawn, NJ). Ultralow-sulfur diesel (USLD) fuel without any lubricity additive was obtained from Chevron Phillips.

Refractive Index and Density

The refractive index was determined on an Abbe 3T refractometer (Attago, Inc., Bellevue, Washington) held at 20 °C with a constant temperature water bath. Density was determined by precisely measuring the weight of desired carbonate in a 1 mL volumetric flask calibrated for the same volume of water at 22.0 °C. The refractive index and density were determined in triplicate.

Viscosity

Kinematic viscosity was determined in accordance with ASTM method D445 [17]. Samples were run in triplicate and a mean viscosity determined.

Melting Point

Melting points were measured by differential scanning calorimetry (DSC) using a DSQ 2000 from T.A. Instruments (Wilmington, DE) following AOCS method CJ 1–94.

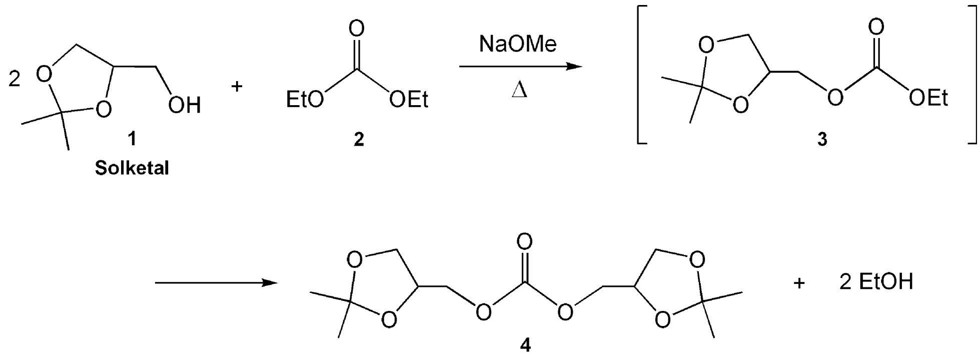
NMR Spectroscopy

^{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 acetone-d_6 or $CDCl_3$ (Cambridge Isotope Laboratories, Andover, MA) as the solvent.

FTIR Spectroscopy

IR spectra were obtained using a Perkin Elmer (Norwalk, CT) Spectrum RX FT-IR system as a liquid film on NaCl plates.

Scheme 1 Carbonate interchange reaction between solketal **1** and diethyl carbonate **2** to give solketal carbonate **4**. 211 × 139 mm (300 × 300 DPI)



Solketal Carbonate ($C_{13}H_{22}O_7$)
Molecular Weight: 290.310
Density (g/cm^3): 1.1496
Refractive Index $n_D^{20°C}$: 1.4460
Melting point (°C): < -50
Kinematic Viscosity (mm^2/s): 26.7 @ 40 °C

GC

GC was performed with a Hewlett Packard 5890 Series gas chromatograph (Palo Alto, CA), equipped with a flame-ionization detector and an autosampler. Analyses were conducted on a HP-5 capillary column, 30 m × 0.32 mm i.d. × 0.25 μm film thickness (Hewlett Packard). Column flow was 3.6 mL/min with helium head pressure of 698 Torr; split ratio of 100:1. The oven temperature program was 100 °C for 2 min, ramp 100–240 °C at 10 °C/min, and then held 20 min at 240 °C. Injector and detector temperatures were set at 280 °C.

High Performance Liquid Chromatography

Samples were analyzed by high performance liquid chromatography (HPLC) on a silica phase Dynamax (250 mm × 4.6 mm, 60 Å, 8 μm) column (Varian, Walnut Creek, CA). A 20 μL injection of sample was eluted from the column with a 40:60 hexane:acetone mixture at 1 mL/min. Sample detection was performed using an evaporative light scattering detector (ELSD, Altech, Deerfield, IL) with the drift tube temperature at 52 °C and nebulizer set at 20 psi (138 kPa) N_2.

GC/MS

GC/MS analyses were conducted using a Hewlett Packard 5890 Series II Plus GC (column: HP-5MS column 30 m × 0.25 mm i.d.; Hewlett Packard Co., Palo Alto, CA) coupled with a Hewlett Packard 5989B mass spectrometer using a mass range of 50–550 AMU. Electron ionization (EI) was performed at 70 eV, whereas positive chemical ionization (CI) used methane as reagent gas. GC conditions: helium head pressure 155 Torr; injector temperature set at 250 °C; transfer line temperature set at 280 °C.

Lubricity

The lubricity of carbonate **4** at 25 and 60 °C was investigated using a high frequency reciprocating rig (HFRR) lubricity testing apparatus (PCS instruments, London, England) as previously described following standard method ASTM D6079 [19]. All samples were run in duplicate.

Preparation of Bis[(2,2-dimethyl-1,3-dioxolan-4-yl)methyl] Carbonate, 4 (Solketal Carbonate)

In a three-neck round bottom flask equipped with a thermometer, magnetic stir bar and a fractionating column connected to a distillate receiver, a solution of solketal (19.56 g, 145.0 mmol) and diethyl carbonate (7.22 g, 59.9 mmol) was prepared. To the stirred solution, sodium methoxide (63.8 mg, 1.18 mmol) was added, and the mixture heated at 85–90 °C under a slight positive N_2 pressure. Reaction progress was monitored by taking aliquots of the reaction mixture at various time points and analyzing them by GC. After 20 h, the reaction temperature was raised to 115–125 °C and an azeotropic mixture of ethanol/diethyl carbonate was distilled. The reaction mixture was cooled, taken up in CH_2Cl_2 (60 mL), washed with H_2O (3 × 25 mL), and then saturated NaCl (1 × 30 mL). The combined CH_2Cl_2 extracts were dried ($MgSO_4$), filtered, and concentrated in vacuo on a rotary evaporator to give 16.0 g of crude golden brown oil. Kugelrohr distillation (90–95 °C/115 mTorr) gave 11.3 g (65%) of **4** as a colorless oil. ^{1}H NMR (acetone-d$_6$) of **4**: δ 4.33 (*m*, 2H, –C*H*–), 4.19 (*dd*, 2H, $J = 11.3$, 4.7 Hz, –C*H*$_2$CO$_3$–), 4.13 (*dd*, 2H, $J = 11.2$, 5.9 Hz, –C*H*$_2$CO$_3$–), 4.08 (*dd*, 2H, $J = 8.5$, 6.5 Hz, –OC*H*$_2$CH(O)–), 3.75 (*dd*, 2H, $J = 8.5$, 5.9 Hz, –OC*H*$_2$CH(O)–), 1.35 (*s*, 6H, –C*H*$_3$), 1.29, (*s*, 6H, –C*H*$_3$). ^{13}C NMR (acetone-d$_6$): δ 155.81 (carbonate C=O), 110.19 (ketal carbon), 74.38 (–*C*H–), 68.92, 68.90, 66.73, 27.08 (–*C*H$_3$), 25.69 (–*C*H$_3$). ^{1}H NMR (CDCl$_3$) δ 4.30 (*m*, 2H, –C*H*(O)–), 4.14 (*d*, 4H, $J = 5.5$ Hz, –C*H*$_2$CO$_3$–), 4.05 (*dd*, 2H, $J = 8.6$, 6.4 Hz, –OC*H*$_2$CH(O)–), 3.75 (*dd*, 2H, $J = 8.6$, 5.8 Hz, –OC*H*$_2$CH(O)–), 1.40 (*s*, 6H, –C*H*$_3$), 1.34, (*s*, 6H, –C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 154.82 (carbonate C=O), 109.91, 73.20, 68.10, 68.07, 66.26, 26.67, 25.30. IR (NaCl) cm^{-1}: 2,988, 2,939, 2,889, 1,753.1 (C=O), 1,456, 1,282, 1,372, 1,251, 1,218, 1,159, 1,086, 1,057, 977, 841, 789. MS (EI): *m*/*z* 291 (MH$^+$, 1%), 275 ([M–CH$_3$]$^+$, 11%), 115 ($C_6H_{11}O_2^+$, 100%), and 101 ($C_5H_9O_2^+$, 34%). MS (CI): *m*/*z* 291 (MH$^+$, 1%), 275 ([M–CH$_3$]$^+$, 11%), 233 ([M–C$_3$H$_5$O]$^+$, 14%), 175 ($C_7H_{11}O_5^+$, 6%), 115 ($C_6H_{11}O_2^+$, 100%).

Preparation of Bis(2,3-dihydroxypropyl) Carbonate **6**

To a solution of solketal carbonate, **4**, (295.6 mg, 1.02 mmol) in 90% methanol (5.50 mL) was added Amberlite IR-120(plus) acidic ion exchange resin (345 mg, 117 w/w% relative to **4**). The reaction mixture was stirred with a magnetic stir bar at 30 °C and reaction progress monitored by HPLC. When the reaction was complete, the resin beads were removed by filtration and the reaction mixture was concentrated in vacuo by rotary evaporator at 25 °C. The residue was taken up in acetone (25 mL), dried with (Na$_2$SO$_4$), filtered, and concentrated again by rotary evaporator without heating to give a clear viscous oil that was dried under vacuum at 22 °C overnight (180 mg, 84%). Silica gel chromatography eluting with 40:60 hexane:acetone gave an enriched sample of carbonate polyol **6**. ^{1}H NMR (acetone-d$_6$) of **6** ($\sim$88% pure; $\sim$12% glycerol impurity): δ 4.20 (*dd*, 2H, $J = 11.0$, 4.2 Hz, –O$_3$CC*H*$_2$CH–), 4.11 (*dd*, 2H, $J = 11.0$, 6.5 Hz, –O$_3$CC*H*$_2$CH–), 3.87 (*m*, 2H, –C*H*(OH)–), 3.56 (*d*, 4H, $J = 5.6$ Hz, –C*H*$_2$OH). ^{13}C NMR: δ 156.12 (carbonate C=O), 70.70 (methine carbon), 69.87 (–*C*H$_2$CO$_3$–), 63.78 (–*C*H$_2$OH). IR (NaCl) cm^{-1}: 3,400 (OH), 2,955, 2,889, 1,736 (C=O), 1,248, 1,039.

Results and Discussion

Preparation of Solketal Carbonate **4**

The carbonate interchange reaction of glycerol with ethylene carbonate or a dialkyl carbonate is a typical method to obtain the 5-membered ring, glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one). As shown in Scheme 1, a carbonate interchange reaction between a mixture of solketal, **1**, and diethyl carbonate, **2**, using sodium methoxide (0.8 mol% relative to solketal) as catalyst gave solketal carbonate, **4**. Because two of the hydroxyl groups of glycerol are protected by the isopropylidene group, cyclization to glycerol carbonate was precluded. By using a molar excess of solketal (2.5:1), the reaction proceeded smoothly and reaction progress was conveniently monitored by GC. The early time aliquots of the reaction mixture showed the concurrent formation of unsymmetrical and symmetrical carbonates, **3** and **4** in roughly equal proportions. The unsymmetrical carbonate **3** was not isolated from the reaction mixture but its identity was established by GC/MS analyses. As the reaction progressed, the unsymmetrical carbonate was converted into the desired symmetrical solketal carbonate, **4**. After 20 h, the crude reaction mixture was shown to contain 70.3% of the desired solketal carbonate **4**, 9.2% mixed ethyl solketal carbonate **3**, 16.3% of the starting solketal alcohol **1**, along with a total of 4.2% of several unidentified impurities by GC. Under the reaction conditions utilized good overall conversion (79.5%) to the carbonates (**3** + **4**) was observed with a selectivity of approximately 88% (70.3% solketal carbonate/79.5% overall conversion to carbonates) to carbonate **4**. The high percentage of **4** obtained under these reaction conditions suggest that steric influences imparted by the solketal's bulky isopropylidene moiety were of little influence during the carbonate interchange reaction as has been previously noted for other sterically encumbered alcohols [11].

Subsequent distillation under reduced pressure gave carbonate **4** as a pure compound for which some physical properties such as density, refractive index, melting point, and viscosity were determined, Scheme 1. The melting point of solketal carbonate **4** was found to be lower than −50 °C. The good low temperature properties were anticipated since solketal, **1**, melts at −26.4 °C and the two bulky isopropylidene groups in carbonate **4** were expected to act synergistically to prevent tight molecular packing that would lead to crystallization and poor low temperature properties. The introduction of alkyl branching in long-chain oleochemical carbonates was previously shown an effective method to improve their low temperature properties [19]. The observed refractive index (1.4460 at 20 °C) of carbonate **4** was similar to the refractive indices determined for the linear and branched oleochemical carbonates, although, the density of carbonate **4** (1.1496 g/cm^3) was significantly higher than the density of linear and branched oleochemical carbonates (0.870–0.895 g/cm^3) and more closely approximated the density of glycerol (1.263 g/cm^3 at 20 °C) [19]. The kinematic viscosity of **4**

(26.7 mm^2/s at 40 C) was determined in the same way as previously reported fatty compounds and found to be higher than that of fatty acid methyl esters [20] and linear (4.9–19.6 mm^2/s) and branched (4.4–22.1 mm^2/s) oleochemical carbonate viscosities determined at the same temperature [19]. Previous work has shown that alkyl branching reduces viscosity [19, 21] and one would expect the isopropylidene methyl groups in carbonate **4** to effectively lower its viscosity. In contrast, the high viscosity of **4** suggest additional factors, such as the presence of oxygen ether atoms, are at play that negate the effect of branching.

NMR Assignment of Solketal Carbonate 4

Figure 1 depicts the ^1H NMR of solketal carbonate **4** in the region 1.15–4.3 ppm in deuterated acetone and the inset structure denotes the hydrogen and carbon assignments made for structure **4**. To clarify the hydrogen and carbon atom assignments, distortionless enhancement by polarization transfer (DEPT), 2D homo-, and heteronuclear correlations were acquired. From these experiments, the multiplet at 4.33 ppm clearly corresponded to the cyclic methine hydrogen. To determine which sets of the doublet of doublet signals observed at 4.13, 4.19, 4.08, and 3.75 ppm cross correlated to one another, 2D homonuclear correlation spectroscopy (COSY) experiments were performed. Analyses of these experiments showed the set of signals at 4.13 and 4.19, and 4.08 and 3.75 ppm, respectively, to be coupled with one another. Using 2D heteronuclear multiple bond correlation (HMBC) experiments, the signals at 4.13 and 4.19 ppm were assigned to the methylene hydrogens adjacent to the carbonate group as these hydrogen signals had a strong three-bond correlation to the carbonyl carbon signal at 155.81 ppm and a two-bond correlation to the methine carbon at 74.38 ppm. Based on the analysis of HMBC experiments the remaining hydrogen signals at 4.08 and 3.75 ppm were assigned to the cyclic methylene hydrogens. These hydrogen signals had a strong three-bond correlation to the carbon signals at 68.92 and 68.90 ppm corresponding to the carbon atom adjacent to the carbonate group and a two-bond correlation with the methine carbon at 74.38 ppm. The isopropylidene methyl group hydrogens were observed as singlets at 1.35 and 1.29 ppm. Interestingly, when the ^1H NMR spectra of solketal carbonate **4** was obtained in $CDCl_3$ instead of deuterated acetone, the signals corresponding to the methylene hydrogens adjacent to the carbonate group coalesced together. This doublet had a chemical shift at 4.14 ppm ($J = 5.5$ Hz) and an integral value corresponding to four hydrogens (see "Experimental procedures").

Assignment of carbon atom signals observed in the ^{13}C NMR spectra (not shown) of solketal carbonate **4** was accomplished using 2D heteronuclear and DEPT NMR experiments. These assignments are shown in Fig. 1. As found for the linear oleochemical carbonates, the chemical shift for the carbonate carbon of **4** (154.8 ppm) was considerably upfield to typical triglyceride ester carbonyl signals (173–175 ppm) but quite similar to the carbonate carbon signal observed for long-chain linear and branched oleochemical carbonates [10]. The carbon atom adjacent to the carbonate group gave two nearly overlapping signals at 68.90 and 68.92 ppm. No explanation for this observation is immediately apparent but these two carbon atoms must experience sufficiently different magnetic environments to cause this unexpected chemical shift splitting.

MS of Solketal Carbonate 4

Electron impact (EI) GC/MS confirmed the structure of solketal carbonate, **4**. A small $[M + H]^+$ molecular ion at *m/z* 291 was observed. Cleavage of the bond between the carbonate oxygen atom and the adjacent methylene carbon atom gave a large fragment ion at *m/z* 115 as the base peak corresponding to the $C_6H_{11}O_2$ fragment. Chemical ionization (CI) GC/MS further confirmed the structure of **4** by giving a $C_7H_{11}O_5^+$ fragment ion at *m/z* 175 corresponding to a fragment containing the carbonate moiety.

Lubricity

Lubricity was assessed using a high-frequency reciprocating rig lubricity (HFRR) tester (ASTM D-6079). Table 1 shows the HFRR lubricity data obtained for the neat solketal carbonate, **4**, and when blended with low-lubricity ultra-low sulfur diesel fuel (ULSD) at 1% level. The maximum acceptable wear scar values on the steel ball used in the HFRR test are 520 or 460 μm at 60 °C in the petrodiesel standards ASTM D975 and EN 590, respectively. The wear scars observed for neat solketal carbonate at 60 °C were slightly larger than those formed at 25 °C but the low wear scar values at both temperatures suggest the neat solketal carbonate has very good lubricity properties and were comparable to the lubricity of linear and branched long-chain oleochemical carbonates (wear scars values ranging from 120 to 256 μm at 25 °C and 313–411 μm at 60 °C) [19]. The influence of various oxygen, nitrogen, and sulfur-substituted compounds on the lubricity of hydrocarbon chains was previously investigated [22]. Lubricity of oxygenated moieties was enhanced in the following general order: COOH > CHO > OH > CO-OCH_3 > C=O > C–O–C. From previous work on linear and branched long-chain oleochemical carbonates, it was shown the lubricity of the carbonate moiety is slightly

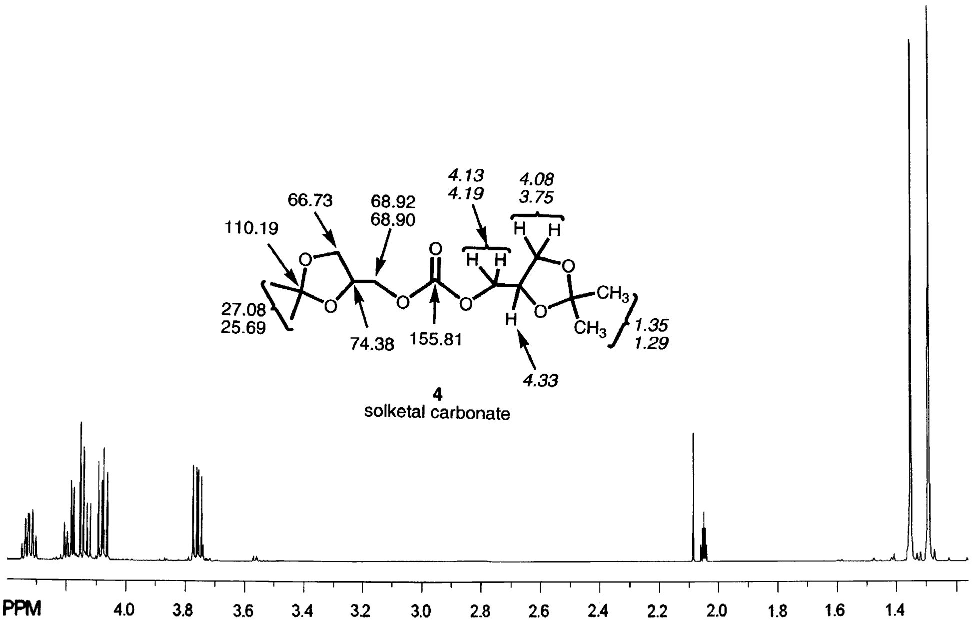


Fig. 1 ^{1}H NMR spectra of solketal carbonate **4** in acetone-d_6 and ^{1}H- and ^{13}C NMR chemical shift assignments (ppm; ^{1}H shifts are *italicized*)

Table 1 HFRR data (wear scar in µm) of solketal carbonate **4**

Material	Wear scar (µm)						Film (%)		Friction	
	25°C			60°C			25°C	60°C	25°C	60°C
	X	*Y*	Average	*X*	*Y*	Average				
ULSD	634, 629	592, 604	613, 617	666, 649	635, 623	651, 636	17, 21	12, 11	0.371, 0.360	0.383, 0.413
Solketal carbonate	160, 159	97, 90	129, 125	199, 165	163, 164	181, 165	100, 100	100, 100	0.113, 0.116	0.126, 0.123
1% Solketal carbonate in ULSD	ND	ND	ND	619, 593	570, 564	595, 579	ND	14, 13	ND	0.305, 0.310

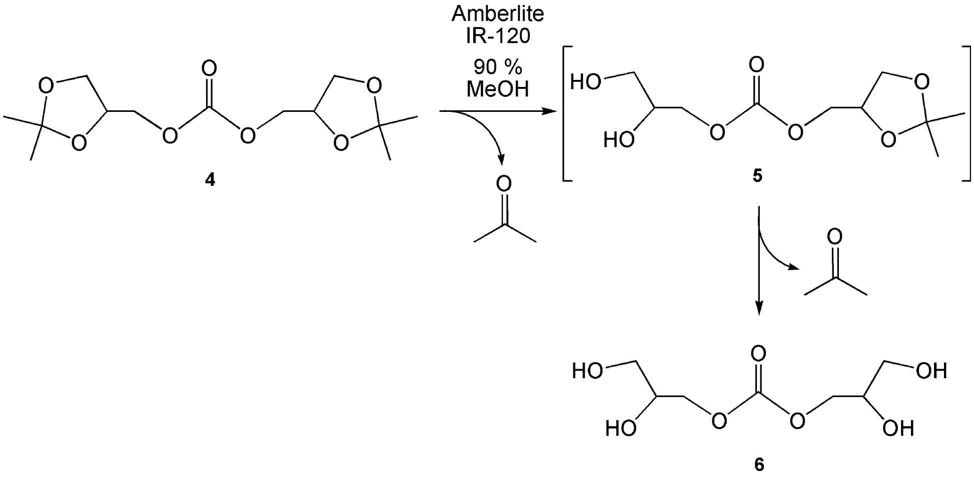
better than neat methyl esters and solketal carbonate appears to follow this trend [19]. The lubricity properties of solketal carbonate are attributed mainly to the carbonyl group. In agreement with previous findings [22], the presence of the four carbon oxygen ether linkages in carbonate **4** does not appear to contribute to the lubricity beyond that of the carbonate moiety alone. The lubricity of ULSD containing 1% solketal carbonate was also examined. As found for the linear and branched long-chain oleochemical carbonates, solketal carbonate at the 1% level did not impart acceptable lubricity to the ULSD, Table 1.

Preparation of Polyol Carbonate 6

Attention was next turned to the removal of the isopropylidene groups of solketal carbonate **4** by acid hydrolysis to produce polyol carbonate, **6**, as shown in Scheme 2. Polyol carbonate **6** was of interest for the preparation of novel carbonate-based ester compounds or as a polyol precursor for the synthesis of carbonate-containing polymers. Treatment of solketal carbonate **4** with an acidic ion exchange resin in 90% MeOH at 30 °C following a modified procedure of Park and coworkers [23] effectively removed the isopropylidene groups. The progress of this reaction was monitored by HPLC over the course of the reaction. During the initial stages of the reaction, the formation of two new peaks at 6.5 and 22.3 min were observed in the HPLC chromatograms in addition to the starting solketal carbonate peak at 3.5 min. The peak at 6.5 min was presumed to be carbonate **5**, wherein, one isopropylidene group was removed while the peak at 22.3 min was presumed to be polyol carbonate **6**. After 140 min of reaction time, the peak at 6.5 min had grown to a maximum amount of 16.9% and then decayed to 2.5% by the reaction end.

After 360 min, carbonate **4** was consumed by HPLC analyses. The reaction was stopped, the resin was filtered away from the reaction solvent, and the solvent was removed by rotovap at 25 °C to give 84% yield of a viscous liquid. Analysis of the crude material by ^{1}H

Scheme 2 Hydrolysis of solketal carbonate **4** to give polyol carbonate **6**. 220 × 141 mm (300 × 300 DPI)

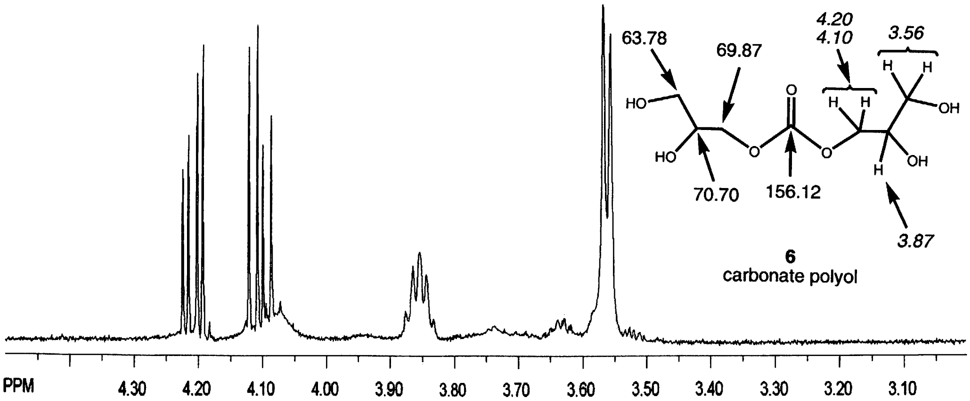


NMR showed the reaction product to be a mixture of compounds composed predominantly of polyol carbonate **6** (~74%), glycerol (~12%), glycerol carbonate (~11%), and a small amount of what was presumed to be partially deprotected carbonate **5** (~3.0%) since HPLC analysis showed carbonate **4** to be absent. The identities of glycerol and glycerol carbonate in the crude reaction mixture were confirmed by comparison of their ^{1}H- and ^{13}C NMR spectra to that of the crude reaction mixture. The presence of glycerol and glycerol carbonate in the crude reaction product likely resulted from intramolecular cyclization of polyol carbonate **5** to produce glycerol carbonate and glycerol during the reaction or work-up. In fact, attempts to monitor the reaction progress using GC and attempts to purify polyol carbonate **6** by vacuum distillation resulted in total decomposition of **6** and the formation of mixtures containing predominantly glycerol carbonate and glycerol. Silica gel chromatography gave an enriched sample of **6** (~88% by HPLC) containing approximately 12% glycerol that was free from the residual partially deprotected carbonate **5** and glycerol carbonate.

NMR Assignment of Polyol Carbonate 6

Figure 2 depicts the ^{1}H NMR of solketal carbonate **6** in the region 3.0–4.5 ppm in deuterated acetone. As for the solketal carbonate **4**, DEPT, 2D homo-, and -heteronuclear correlations were acquired to unambiguously assign the hydrogen and carbon atoms. The inset structure shown in Fig. 2 denotes the hydrogen and carbon assignments made for the structure of **6** using these NMR techniques. The multiplet at 3.87 ppm corresponded to the methine hydrogen. The two sets of doublet of doublet signals at 4.20 and 4.11 ppm were found to correlate to each other and were subsequently assigned to the hydrogens adjacent to the carbonate group. The remaining signal at 3.56 ppm observed as a doublet had an integral value corresponding to four hydrogens and was assigned to the methylene hydrogens of the carbons attached to the primary hydroxyl groups. The ^{13}C NMR spectra had four signals corresponding to the carbon atoms of **6** which were readily assigned utilizing the various 1D- and 2D NMR techniques. The assignment of the carbon atoms is shown on the inset structure in Fig. 2.

Fig. 2 ^{1}H NMR spectra of polyol carbonate **6** in acetone-d_6 and ^{1}H- and ^{13}C NMR chemical shift assignments (ppm; ^{1}H shifts are *italicized*)



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