Synthesis and Characterization of Dialkyl Carbonates Prepared from Mid-, Long-Chain, and Guerbet Alcohols

James A. Kenar*, Gerhard Knothe, and Ashley L. Copes

Food and Industrial Oil Research, NCAUR, ARS, USDA, Peoria, Illinois 61604

ABSTRACT: A series of organic carbonates derived from mid-, long-chain, and Guerbet alcohols were synthesized in good yields (69–80% isolated yields after purification by distillation or recrystallization) through a carbonate interchange reaction by heating the linear or Guerbet alcohols with diethyl carbonate in the presence of catalyst, *n*-dibutyltin oxide. The carbonates were isolated by Kügelrohr distillation or recrystallization from acetone and characterized using FTIR, GC, ^{1}H and ^{13}C NMR spectroscopy, and GC–MS. EI and positive CI mass-spectral techniques were used to characterize the carbonates. Such materials are currently of commercial interest as lubricants and additives in various industrial applications.

Paper no. J10742 in *JAOCS 81*, 285–291 (March 2004).

KEY WORDS: Carbonate interchange reaction, dialkyl carbonates, fatty alcohols, Guerbet alcohols, Guerbet carbonates, long-chain carbonates, mass spectrometry, nuclear magnetic resonance.

Dialkyl carbonates are generally safe noncorrosive molecules employed in numerous commercial and synthetic applications (1–3). For example, short-chain dialkyl carbonates such as dimethyl and diethyl carbonate are currently being evaluated as oxygen-containing additives to reduce exhaust emissions in gasoline and diesel engines (4). Both diethyl and dimethyl carbonates are gaining popularity as nontoxic replacements for hazardous chemical reagents such as phosgene and dimethyl sulfate (5). Recently, Rüsch gen. Klaas and Warwel (6) showed that dimethyl and diethyl carbonates can be used as reactive solvents to simultaneously extract and transesterify oilseed oils.

Longer-chain and branched (Guerbet) dialkyl carbonates also may find application in lubricant (7,8), cosmetic (9,10), plasticizer (11), and fuel (12) compositions. In the case of dialkyl carbonate-based lubricants, the carbonate group is postulated to interact with metallic surfaces, and tribological testing has shown them to have oiliness properties comparable to or better than mineral oil and traditional synthetic esters with the same viscosities, as well as better seal compatibility (3).

The excellent properties and apparent commercial applications of dialkyl carbonates have led to a sizable body of patent literature reporting dialkyl carbonate syntheses (1,2). Some of the better-known methods of preparing dialkyl carbonates include oxidative carbonylation of alcohols with carbon monoxide (13); reaction of alcohols with phosgene (14); reaction of urea with alcohols in the presence of metal salt catalysts (15); and reaction of alkyl halides with metal carbonate salts such as K_2CO_3 or $KHCO_3$ (16). More recently, carbonate interchange reactions between small-chain dialkyl carbonates and alcohols have received much attention (17). Dialkyl carbonates also have been prepared enzymatically using lipases (18,19). Although proprietary work has been carried out using various dialkyl carbonates, to our knowledge, a systematic analytical characterization, especially of linear longer-chain and branched dialkyl carbonates, is not available.

In the present work, nine linear and branched dialkyl carbonates were prepared in good yields through a carbonate interchange reaction between various mid-, long-chain, or Guerbet alcohols and diethyl carbonate using dibutyltin oxide as catalyst. The carbonates were subsequently characterized by ^{1}H and ^{13}C NMR, FTIR, as well as EI and positive CI GC–MS.

EXPERIMENTAL PROCEDURES

Materials. All chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without further purification unless otherwise noted. Oleyl alcohol (85% technical grade, Aldrich) was found to contain approximately 20% *trans*-isomer as determined by integration of the *cis*- (5.35–5.39 ppm) and *trans*- (5.31–5.35 ppm) olefinic hydrogen signals in the NMR spectra. Methylene chloride was obtained from Fisher Scientific Co. (Fairlawn, NJ). Isolauryl (2-butyloctanol, Jarcol I-12) and isocetyl (2-hexyldecanol, Jarcol I-16) alcohols were obtained from Jarchem Industries, Inc. (Newark, NJ).

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

NMR. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker ARX 400 spectrometer (Billerica, MA) with a 5-mm dual proton/carbon probe (400 MHz ^{1}H/100.61 MHz ^{13}C) using $CDCl_3$ as the solvent in all experiments.

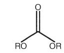
FTIR. IR spectra were obtained using a PerkinElmer (Norwalk, CT) Spectrum RX FTIR system as either a film on NaCl plates (liquids) or in a KBr matrix (solids).

GC. GC was performed with a Hewlett-Packard 5890 Series II gas chromatograph (Palo Alto, CA), equipped with an FID and an autosampler/injector. Analyses were conducted on an HP-5MS capillary column, 30 m × 0.25 mm i.d. (Hewlett-Packard).

---

*To whom correspondence should be addressed at USDA, ARS, NCAUR, 1815 N. University St., Peoria, IL 61604.
E-mail: kenarja@ncaur.usda.gov

TABLE 1
Reaction Conditions, Yields, and b.p./m.p. of Long-Chain and Guerbet Carbonates 4a–i[a]

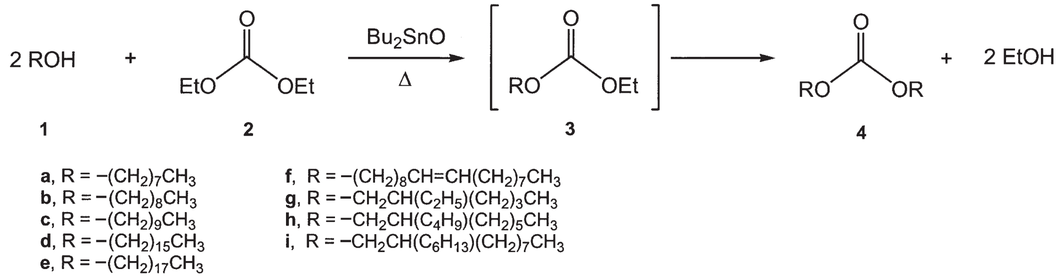
	Temp. (°C)	Time (h)	Yield[b] (%)	b.p. (°C/Torr)	m.p. (°C)
4a, R = $CH_3(CH_2)_7$–	115	24	79.8	100/0.370	—
4b, R = $CH_3(CH_2)_8$–	125	19	77.5	125/0.480	—
4c, R = $CH_3(CH_2)_9$–	120	20	78.8	142/0.140	—
4d, R = $CH_3(CH_2)_{15}$–	120	28	77.8	—	46–47
4e, R = $CH_3(CH_2)_{17}$–	130	25	77.3	—	56–57
4f, R = $CH_3(CH_2)_7CH{=}CH(CH_2)_8$– (*cis*/*trans* *ca.* 3.76:1)	140	24	77.7	195/0.480	—
4g, R = $CH_3(CH_2)_3CH(C_2H_5)CH_2$– (2-ethylhexyl)	140	26	70.6	100/0.500	—
4h, R = $CH_3(CH_2)_5CH(C_4H_9)CH_2$– (2-butyloctyl)	135	24	69.4	140/0.275	—
4i, R = $CH_3(CH_2)_7CH(C_6H_{13})CH_2$– (2-hexyldecyl)	133	24	71.1	185/0.380	—

[a] 0.3–0.9 mol% of Bu_2SnO relative to alcohol was used as catalyst.
[b] Isolated yield of purified dialkyl carbonate.

TABLE 2
^{1}H and ^{13}C NMR Data of Mid-, Long-Chain and Guerbet Carbonates Synthesized in the Present Work

Entry[a]	^{1}H NMR	^{13}C NMR
4a	4.09 (*t*, 4H, *J* = 6.7 Hz), 1.70–1.60 (*m*, 4H), 1.45–1.20 (*m*, 22H), 0.85 (*t*, 6H, *J* = 6.9 Hz)	155.51, 68.08, 31.82, 29.25, 29.21, 28.75, 25.77, 22.69, 14.12
4b	4.03 (*t*, 4H, *J* = 6.7 Hz), 1.60–1.54 (*m*, 4H), 1.30–1.19 (*m*, 24H), 0.80 (*t*, 6H, *J* = 6.9 Hz)	155.39, 67.86, 31.86, 29.48, 29.25, 28.72, 25.73, 22.65, 14.01
4c	4.10 (*t*, 4H, *J* = 6.7 Hz), 1.70–1.60 (*m*, 4H), 1.38–1.20 (*m*, 28H), 0.86 (*t*, 6H, *J* = 6.9 Hz)	155.53, 68.12, 31.96, 29.57, 29.37, 29.30, 28.76, 25.78, 22.75, 14.19
4d	4.10 (*t*, 4H, *J* = 6.7 Hz), 1.70–1.55 (*m*, 4H), 1.40–1.15 (*m*, 52H), 0.87 (*t*, 6H, *J* = 6.8 Hz)	155.53, 68.11, 32.90, 32.01, 29.77, 29.75, 29.64, 29.57, 29.52, 29.44, 29.31, 28.76, 25.78, 22.77, 14.19
4e	4.11 (*t*, 4H, *J* = 6.7 Hz), 1.70–1.55 (*m*, 4H), 1.40–1.15 (*m*, 60H), 0.87 (*t*, 6H, *J* = 6.8 Hz)	155.53, 68.12, 32.01, 29.77, 29.75, 29.72, 29.64, 29.57, 29.44, 29.31, 28.77, 25.79, 22.77, 14.20
4f	5.40–5.29 (*m*, 4H, *cis* + *trans*), 4.08 (*t*, 4H, *J* = 6.7 Hz), 2.00–1.85 (*m*, 8H), 1.63–1.55 (*m*, 4H), 1.27–1.23 (*m*, 44H), 0.85 (*t*, 6H, *J* = 6.9 Hz)	155.46, 130.44, 130.24, 129.98, 129.79, 68.03, 32.61, 31.92, 29.78, 29.73, 29.67, 29.53, 29.50, 29.40, 29.33, 29.21, 29.14, 29.05, 28.70, 27.22, 27.19, 25.71, 22.69, 14.11
4g	3.99 (*d*, 4H, *J* = 6.00 Hz), 1.60–1.50 (*m*, 2H), 1.35–1.23 (broad *m*, 16H), 0.87–0.83 (*m*, 12H)	155.78, 70.33, 38.91, 30.17, 28.91, 23.53, 22.98, 14.02, 10.89
4h	4.01 (*d*, 4H, *J* = 5.95 Hz), 1.70–1.57 (broad *m*, 2H), 1.34–1.23 (broad *m*, 32H), 0.86 (*m*, 12H)	155.80, 70.77, 37.50, 31.87, 31.06, 30.73, 29.66, 28.93, 26.69, 23.02, 22.70, 14.11, 14.06
4i	4.01 (*d*, 4H, *J* = 5.94 Hz), 1.70–1.60 (broad *m*, 2H), 1.28–1.24 (broad *m*, 48H), 0.86 (*m*, 12H)	155.82, 70.82, 37.53, 31.97, 31.88, 31.05, 30.01, 29.67, 29.63, 29.38, 26.73, 26.70, 22.74, 22.71, 14.14

[a] Entry numbers correspond to Scheme 1.



SCHEME 1

The column flow was 1.0 mL/min with helium head pressure of 15 psi (776 torr); split ratio of 75:1. Two different oven temperature ramp programs were utilized: Program A, 100°C for 2 min, ramp 100–270°C at 20°C/min, hold 20 min at 270°C. Program B, 140°C for 2 min, ramp 140–280°C at 20°C/min, hold 30 min at 280°C. Injector and detector temperatures were set at 280°C.

GC–MS. GC–MS analyses were conducted using a Hewlett-Packard 5890 Series II Plus GC (HP-5MS column, 30 m × 0.25 mm i.d.; Hewlett-Packard) coupled with a Hewlett-Packard 5989B mass spectrometer using a mass range of 50–550 amu. EI was performed at 70 eV, whereas positive CI used methane as reagent gas. GC conditions: helium head pressure 3 psi (155 torr); injector temperature set at 250°C; transfer line temperature set at 280°C. The two oven temperature ramp programs described in the GC experimental section were utilized for GC–MS studies.

Carbonate purification. Solid materials were recrystallized by dissolving material in warm acetone. Upon cooling to room temperature, white crystals formed that were collected by vacuum filtration. Liquid materials were distilled *in vacuo* using a Kügelrohr distillation apparatus.

Representative procedure for the synthesis of linear and branched dialkyl carbonates. Synthesis of nonyl carbonate ***4b*** *(17).* In a three-necked round-bottomed flask equipped with a magnetic stir bar and reflux condenser, a mixture of nonyl alcohol (93.6 g, 0.64 mol) and dibutyltin oxide (807.6 mg, 0.0032 mol, 0.5 mol% relative to alcohol) was heated to 80–95°C under a slight positive nitrogen pressure. When the dibutyltin oxide catalyst dissolved in the alcohol, diethyl carbonate (37.9 g, 0.32 mol) was added dropwise over approximately 30 min. The flask temperature was then raised to 125°C and refluxed 19 h. Reaction progress was monitored by taking aliquots of the reaction mixture at various time points and analyzing them by GC. When deemed complete, the reaction mixture was taken up in CH_2Cl_2 (100 mL) and washed with H_2O (3 × 50 mL). The combined CH_2Cl_2 extracts were dried ($MgSO_4$), filtered through a pad of Celite®, and concentrated *in vacuo* on a rotary evaporator. The crude product was then placed under vacuum overnight at 22°C. GC analyses of the resulting crude pale yellow oil showed the following relative amounts: starting alcohol (9%), mixed ethyl nonyl carbonate (<1%), and desired nonyl carbonate (90%). The identification of each compound was verified by GC–MS. Kügelrohr distillation (125°C/0.48 mTorr) gave 78.0 g of **4b** (entry **4b** in Tables 1 and 2) as a colorless distillate (77.5%). Tables 1 and 2 contain specific information on reaction conditions, product yields, and characterization data for each of the products prepared.

RESULTS AND DISCUSSION

Scheme 1 depicts the dialkyl carbonate interchange reaction sequence utilized to synthesize the linear and branched carbonates, **4**, prepared in this study. By using a modified procedure of Shaikh and Sivaram (17), alcohol **1** was reacted with diethyl carbonate, **2**, under neat conditions using dibutyltin oxide (0.3–0.9 mol% relative to alcohol **1**) as catalyst. Although many catalysts are known to catalyze the dialkyl carbonate interchange reaction (1,8), dibutyltin oxide was chosen in favor of other catalysts based on the work of Shaikh and Sivaram (17) that showed dibutyltin oxide to be an effective catalyst for the synthesis of dialkyl carbonates. Our reactions proceeded smoothly, and although literature reports suggest GC analyses

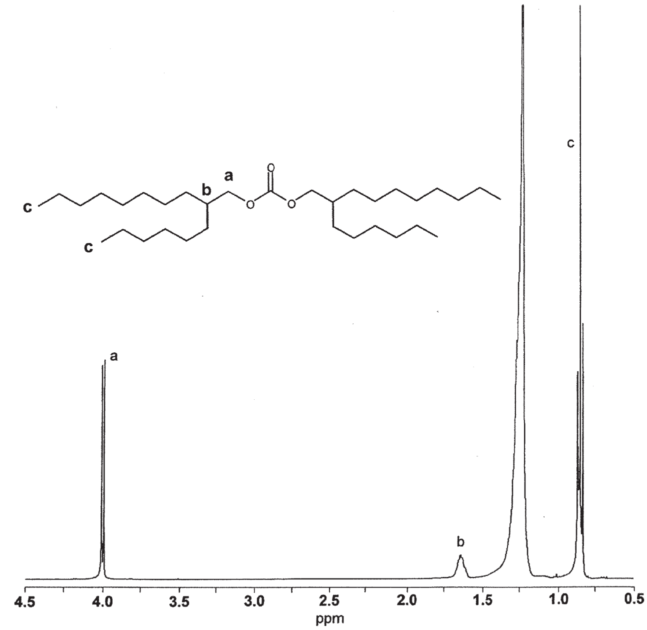
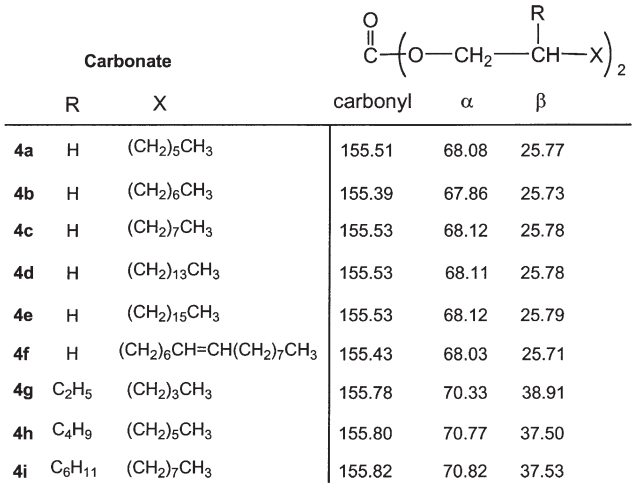


FIG. 1. 400 MHz ^1H NMR spectrum of 2-hexyldecyl carbonate, **4i**, in $CDCl_3$. Peak assignments are designated by the letters **a**, **b**, and **c**.



$$\overset{O}{\overset{\|}{C}}\left(O-CH_2-\overset{R}{\overset{|}{CH}}-X\right)_2$$

Carbonate	R	X	carbonyl	α	β
4a	H	$(CH_2)_5CH_3$	155.51	68.08	25.77
4b	H	$(CH_2)_6CH_3$	155.39	67.86	25.73
4c	H	$(CH_2)_7CH_3$	155.53	68.12	25.78
4d	H	$(CH_2)_{13}CH_3$	155.53	68.11	25.78
4e	H	$(CH_2)_{15}CH_3$	155.53	68.12	25.79
4f	H	$(CH_2)_6CH=CH(CH_2)_7CH_3$	155.43	68.03	25.71
4g	C_2H_5	$(CH_2)_3CH_3$	155.78	70.33	38.91
4h	C_4H_9	$(CH_2)_5CH_3$	155.80	70.77	37.50
4i	C_6H_{11}	$(CH_2)_7CH_3$	155.82	70.82	37.53

FIG. 2. Assignment of the characteristic ^{13}C NMR carbonate signals.

of smaller carbonates are problematic due to CO_2 liberation upon heating the carbonate (20), the reaction progress of the carbonates in this study was conveniently monitored by GC except for oleyl carbonate **4f** (oven temperature program A was used for carbonates **4a–c** and **4g**, whereas oven temperature program B was used for **4d,e,h,i**). Oleyl carbonate was problematic and gave poor GC results. The reasons for this are not presently clear and may result either from its nonvolatility or possible side reactions occurring at the unsaturated sites of the molecule under the GC conditions tried.

During the early-time aliquots of the reactions, unsymmetrical carbonates, **3**, were produced in conjunction with the desired symmetrical carbonates, **4**, in up to 1:1 relative amounts. We did not isolate the unsymmetrical carbonates, but their identities were confirmed by GC–MS analyses. As the reaction progressed, **3** was subsequently converted into the desired carbonate, **4**. Table 1 gives reaction conditions, b.p./m.p. data, and isolated yields obtained for the various dialkyl carbonates synthesized. As can be seen, the carbonates were obtained in yields ranging from 69 to 80% after purification by distillation or recrystallization. IR spectroscopy of all the purified carbonates showed two strong absorptions of interest at 1747 and 1250 cm^{-1}, corresponding to the C=O and C–O stretching frequencies, respectively.

NMR spectroscopy. The ^1H and ^{13}C NMR data for the carbonates synthesized are presented in Table 2 and Figure 2. The ^1H NMR spectra of all the carbonate samples are generally similar, and the spectrum of 2-hexyldecyl carbonate, shown in Figure 1, is representative (Table 2, entry **4i**). The main feature of interest is the doublet at 4.01 ppm. This signal corresponds to the α-methylene hydrogens (designated by "**a**" in Fig. 1) and is split into a doublet by the adjacent β-methine hydrogen (designated by "**b**" in Fig. 1). The corresponding α-methylene hydrogen signals in the linear carbonates **4a–f** are located at approximately the same chemical shift but are split into a triplet owing to the presence of two adjacent β-methylene hydrogens (Table 2). The remaining hydrogen signals in the ^1H NMR show the expected

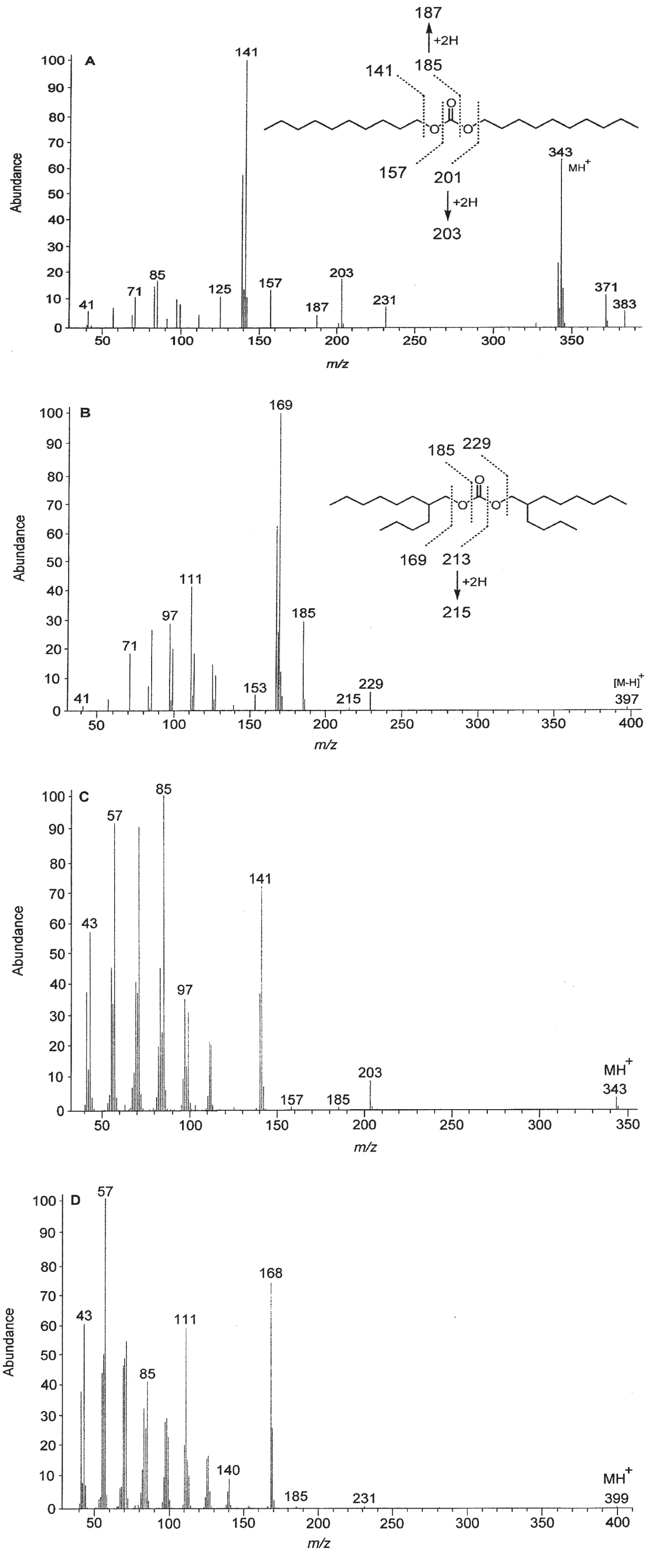


FIG. 3. Positive CI (methane) and EI mass spectra of linear and branched carbonates. (A) CI of decyl carbonate **4c**; (B) CI of 2-butyloctyl carbonate **4h**; (C) EI of decyl carbonate **4c**; (D) EI of 2-butyloctyl carbonate **4h**.

CH_2 and CH_3 peaks, and their integration corresponds to the expected number of hydrogens. In addition to the signals observed for the saturated carbonates, oleyl carbonate, **4f**, also contained

TABLE 3
Positive CI and EI Mass Spectral Data of Mid-, Long-Chain, and Guerbet Carbonates Synthesized in the Present Work

Entry[a]	PCI-MS	EI-MS
4a	327 ($[M + C_3H_5]^+$, 10%), 315 ($[M + C_2H_5]^+$, 15%), 287 (MH^+, 100%), 203 (10%), 175 (25%), 159 (4%), 129 (11%), 113 (84%)	287 (MH^+, 2%), 175 (7%), 157 (1%) 129 (1%), 113 ($[C_8H_{17}]^+$, 48%), 71 (100%)
4b	355 ($[M + C_3H_5]^+$, 7%), 343 ($[M + C_2H_5]^+$, 14%), 315 (MH^+, 66%), 217 (9%), 189 (23%), 173 (3%), 143, 11%), 127 (100%)	315 (MH^+, 1%), 189 (8%), 171 (1%), 143 (1%), 127 ($[C_9H_{19}]^+$, 52%) 71 (100%)
4c	383 ($[M + C_3H_5]^+$, 6%), 371 ($[M + C_2H_5]^+$, 12%), 343 (MH^+, 61%), 231 (8%), 203 (17%), 187 (4%), 157 (14%), 141 (100%)	343 (MH^+, 4%), 203 (9%), 185 (1%), 157 (1%), 141 ($[C_{10}H_{21}]^+$, 69%), 85 (100%)
4d	509 ($[M - H]^+$, 6%), 241 (65%), 225 (100%)	511 (MH^+, 1%), 287 (3%), 225 ($[C_{16}H_{33}]^+$, 49%), 85 (59%), 71 (74%), 57 (100%)
4e	No molecular ion or adducts, 269 (61%), 253 (100%)	No molecular ion, 315 (2%), 253 (55%), 57 (100%)
4f[b]	—	—
4g	287 (MH^+,19%), 285 ($[M - H]^+$, 5%), 173 (21%), 159 (21%), 129 (11%), 113 (100%)	287 (MH^+, 0.2%), 175 (1%), 129 (1%), 112 ($[C_8H_{16}]^+$, 66%), 70 (83%), 57 (100%)
4h	397 ($[M - H]^+$, 1%), 229 (6%), 215 (2%), 185 (29%), 169 (100%)	399 (MH^+, 0.2%), 231 (1%), 185 (1%), 168 ($[C_{12}H_{24}]^+$, 71%), 111 (57%), 57 (100%)
4i	510 (M^+, 1%), 285 (5%), 271 (1%), 241 (32%), 225 (100%)	No molecular ion, 241 (1%), 224 (56%), 111 (50%), 57 (100%)

[a] Entry numbers correspond to Scheme 1.
[b] Oleyl carbonate, **4f**, was not amenable to GC–MS or DIP under the conditions tried. PCI, positive CI; DIP, direct insertion probe.

signals at 5.29–5.40 ppm, corresponding to the hydrogens attached to the olefinic carbons.

The structure of the carbonates with assignments of characteristic ^{13}C signals is given in Table 2 and Figure 2. The ^{13}C NMR spectra of the carbonates display the signal of the carbonate carbons at 155–156 ppm. These shifts are considerably upfield from typical alkyl esters of FA, in which cases the signals of the ester carbons are usually in the 173–175 ppm range. An electron-releasing effect of the additional oxygen atom compensating for electron withdrawal of the carbonyl oxygen has been discussed for the upfield shifts of carboxylic carbons vs. keto carbons (21) and may be responsible for the further upfield shift of the carbonate carbons vs. carboxylic carbons. However, there appears to be a minor difference in the chemical shift of the carbonate carbons depending on the nature of the alkyl chain. In the β-branched carbonates, the carbonate carbon signal is observed at approximately 155.8 ppm, whereas in the case of linear alkyl chains, the signal is found slightly upfield at 155.4–155.5 ppm. The effect of branching is more pronounced in the signals of the α- and β-carbons (see Fig. 2).

The shift of the α-carbons varies from about 68 ppm for linear alkyl chains to 70.3–70.8 ppm for branched alkyl moieties. It is noteworthy that the α-carbon in long-chain di-Guerbet esters (22), which corresponds to the α-carbon in the present compounds, displays its shift slightly upfield (66.5–66.6 ppm) from that of the present carbonates (23). The reason for the differences in the shifts of the α-carbons in the present compounds vs. di-Guerbet esters is likely the additional oxygen atom of the carbonates causing reduced electron density at the α-carbon of the carbonates. The signals of the β-carbons are found at 25.7–25.8 ppm in the unbranched carbonates, but in the branched compounds their shifts are observed at 37.5–38.9 ppm.

There also appears to be an effect of chain length, as the shortest chain in the β-position (2-ethylhexyl carbonate) appears to cause an upfield shift (70.33 ppm) of the α-carbons' signal compared to the longer chains (in 2-butyloctyl and 2-hexyldecyl carbonate) with values around 70.8 ppm. A similar, albeit reverse, chemical shift effect regarding chain length is observed in the β-carbons, which are the branching sites in the branched carbonates. For these β-carbons, the signal in the short-chain ethyl group is observed at 38.91 ppm, but in the case of the longer butyl and hexyl groups, the β-carbon signal is shifted upfield to about 37.5 ppm.

MS. Only a few studies have examined the MS of carbonate molecules, and these have focused mainly on short-chain carbonates (24,25). Both EI and methane positive CI GC–MS were utilized to characterize the dialkyl carbonates prepared here. The four mass spectra depicted in Figure 3 of decyl carbonate (linear) and 2-butyloctyl carbonate (branched) serve to illustrate the important mass spectral features observed in the CI and EI ionization modes. Methane CI, one of the most commonly used alternative ionization techniques, commonly gives abundant product ions from the molecules that are indicative of the M.W. Linear carbonates **4a–c** were no exception, and, as can be seen in the CI mass spectrum of decyl carbonate (Fig. 3A), intense fragment ions at *m/z* 343, 371, and 383 were observed, corresponding to the protonated carbonate, the C_2H_5 adduct, and the C_3H_5 adduct, respectively. Interestingly, the longer C_{16} linear carbonate, **4d**, gave only a $[M - H]^+$ adduct at *m/z* 509, whereas the C_{18} linear carbonate, **4e**, did not give any ions corresponding to the M.W. Table 3 tabulates the distinctive EI and CI fragments for the compounds examined.

Branched carbonates, **4g–i,** did not give any C_2H_5 or C_3H_5 adducts corresponding to the M.W., as can be seen in the CI spectrum of 2-butyloctyl carbonate **4h** (Fig. 3B). Instead, 2-ethylhexyl carbonate **4g** gave a relatively abundant MH^+ molecular ion at *m/z* 287, 2-butyloctyl carbonate **4h** gave a $[M - H]^+$ molecular ion at *m/z* 397, and 2-hexyldecyl carbonate **4i** gave a M^+ molecular ion at *m/z* 510.

The linear and branched carbonates, **4a–c** and **4g–i**, respectively, showed distinctive fragment ions due to cleavage around the carbonate moiety, confirming its presence. For example, the CI spectrum of decyl carbonate, Figure 3A, shows fragment ions at *m/z* 203, 187, 157, and 141 corresponding to $[C_{11}H_{23}O_3]^+$, $[C_{11}H_{23}O_2]^+$, $[C_{10}H_{21}O]^+$, and $[C_{10}H_{21}]^+$, respectively. The fragment ion at *m/z* 203 $[C_{11}H_{23}O_3]^+$ is likely derived from loss of the $C_{10}H_{21}$ alkyl group in conjunction with a rearrangement of two protons, although a McLafferty-type rearrangement of a protonated carbonate molecule is also plausible. Loss of a $C_{10}H_{21}O$ moiety with rearrangement of two protons gives fragment ion *m/z* 187 $[C_{11}H_{23}O_2]^+$. This type of double hydrogen rearrangement for small-chain carbonates has been noted previously (22). The *m/z* 231 ion observed in the CI of decyl carbonate (Fig. 3A) is likely a C_2H_5 adduct of fragment ion *m/z* 202 ($[C_{11}H_{22}O_3]^+$, not observed). A C_2H_5 adduct of this type was also observed in all three carbonates **4a–c**.

The CI mass spectral characteristics for the branched carbonate series **4g–i** are similar to that observed for **4a–c** (Fig. 3B). The fragment ions observed for 2-butyloctyl carbonate **4h** at *m/z* 229, 215, 185, and 169 correspond to cleavage at the same bond locations as observed for linear carbonates, **4a–c**, although the fragment mechanisms appear to be slightly different. Fragment ion *m/z* 229 $[C_{13}H_{25}O_3]^+$ occurs from loss of a $C_{12}H_{25}$ alkyl group without any hydrogen rearrangement, but the fragment ion at *m/z* 215 $[C_{13}H_{27}O_2]^+$ likely results from loss of a $C_{12}H_{25}O$ moiety with rearrangement of two protons. Fragment ions at *m/z* 185 and 169 correspond to $[C_{12}H_{25}O]^+$ and $[C_{12}H_{25}]^+$, respectively. The prominent C_2H_5 adduct observed in the linear carbonates (*m/z* 231 in Fig. 3A) was not observed for any of the branched carbonate molecules.

Generally, the spectra obtained using EI-MS gave similar results. Many of the characteristic fragment ions observed, however, were weaker in intensity, and some of the hydrogen rearrangements seen in the CI spectra did not occur in the EI spectra (Figs. 3C, 3D). The EI spectra also typically gave very weak MH^+ fragment ions, and in fact, no molecular ions were observable for carbonates **4e** and **4i**. Finally, the EI mass spectra of both the linear and branched carbonates gave more intense fragmentation ions at the lower *m/z* ranges due to alkyl chain fragmentation.

Dialkyl carbonates were synthesized from mid-, long-chain, and Guerbet alcohols and characterized by MS and NMR. Both EI and CI gave distinctive fragment ions useful in confirming the identities of the carbonate structures.

ACKNOWLEDGMENTS

The authors thank Joneen McElligott for her help in the preparation of these compounds and Dr. David Weisleder for collection of the NMR data.

REFERENCES

1. Shaikh, A.-A.G., and S. Sivaram, Organic Carbonates, *Chem. Rev. 96*:951–976 (1996).
2. Parrish, J.P., R.N. Salvatore, and K.W. Jung, Perspectives on Alkyl Carbonates in Organic Synthesis, *Tetrahedron 56*:8207–8237 (2000).
3. Fisicaro, G., and G. Gerbaz, Dialkylcarbonates, in *Synthetic Lubricants and High-Performance Functional Fluids*, edited by R.L. Shubkin, Marcel Dekker, New York, 1993, pp. 229–239.
4. Roh, N.-S., B.C. Dunn, E.M. Eyring, R.J. Pugmire, and H.L.C. Meuzelaar, Production of Diethyl Carbonate from Ethanol and Carbon Monoxide over a Heterogeneous Catalytic Flow Reactor, *Fuel Process. Technol. 83*:27–38 (2003).
5. Ono, Y., Dimethyl Carbonate for Environmentally Benign Reactions, *Catal. Today 35*:15–25 (1997).
6. Rüsch gen. Klaas, M., and S. Warwel, Reactive Extraction of Oilseeds with Dialkyl Carbonates, *Eur. J. Lipid Sci. Technol. 103*:810–814 (2001).
7. Ishida, N., H. Hasegawa, U. Sasaki, and T. Ishikawa, Fluid Compositions for Refrigerators, U.S. Patent 5,391,311 (1995).
8. Westfechtel, A., F. Bongardt, and A. Ansmann, Guerbet Carbonates, U.S. Patent 5,387,374 (1995).
9. Ansmann, A., U. Issberner, S. Bruening, B. Jackwerth, and D. Hoffmann, Wax-Based Compositions for the Preparation of Cosmetic Tissues and Wipes, WO Patent 2003005981 (2003).
10. Suetake, T., Oily Solid Cosmetics Containing Dialkyl Carbonates, Japanese Patent 20011328918 (2001).
11. Giolito, S.L., J.C. Goswami, and E.D. Weil, Carbonate Esters, Carbonate Ester Compositions, and Plasticized Compositions, U.S. Patent 4,403,056 (1983).
12. Liotta, F.J., Jr., Process for the Preparation of Unsymmetric Dialkyl Carbonates, U.S. Patent 5,206,408 (1993).
13. Romano, U., R. Tesel, M.M. Mauri, and P. Rebora, Synthesis of Dimethyl Carbonate from Methanol, Carbon Monoxide, and Oxygen Catalyzed by Copper Compounds, *Ind. Eng. Chem. Prod. Res. Dev. 19*:396–403 (1980).

14. Choppin, A.R., and J.W. Rogers, The Preparation of Di-*t*-butyl Carbonate and *t*-Butyl Chlorocarbonate, *J. Am. Chem. Soc. 70*:2967 (1948).
15. Ball, P., H. Fullmann, and W. Heitz, Carbonates and Polycarbonates from Urea and Alcohol, *Angew. Chem. Int. Ed. 19*:718–720 (1980).
16. Lissel, M., and E.V. Dehmlow, Phasentransfer-Katalytische Hersellung von Kohlensäurestern Ohne Verwendung von Phosgen, *Chem. Ber. 114*:1210–1215 (1981).
17. Shaikh, A.-A.G., and S. Sivaram, Dialkyl and Diaryl Carbonates by Carbonate Interchange Reaction with Dimethyl Carbonate, *Ind. Eng. Chem. Res. 31*:1167–1170 (1992).
18. Pioch, D., P. Lozano, and J. Graille, First Lipase-Catalyzed Synthesis of Fatty Carbonate Esters, *Biotechnol. Lett. 13*:633–636 (1991).
19. Poza, M., R. Pulido, and V. Gotor, Vinyl Carbonates as Novel Alkoxycarbonylation Reagents in Enzymatic Synthesis of Carbonates, *Tetrahedron 48*:6477–6484 (1992).
20. Pelet, S., J.W. Yoo, and Z. Mouloungui, Analysis of Cyclic Organic Carbonates with Chromatographic Techniques, *J. High Resolut. Chromatogr. 22*:276–278 (1999).
21. Breitmaier, E., and W. Voelter, *Carbon-13 NMR Spectroscopy*, 3rd edn., VCH, Weinheim, Germany, 1989.
22. Knothe, G., and K.D. Carlson, Synthesis, Mass Spectrometry, and Nuclear Magnetic Resonance Characterization of Di-Guerbet Esters, *J. Am. Oil Chem. Soc. 75*:1861–1866 (1998).
23. Knothe G., Characterization of Esters of Fatty Acids and Diacids with Guerbet Alcohols, *Ibid. 78*:537–540 (2001).
24. Griff, S.P., Structure Determination of Carbonates and Diglycol Carbonates by Gas Chromatography–Mass Spectrometry, *Appl. Spectrosc. 37*:354–357 (1983).
25. Brown, P., and C. Djerassi, Mass Spectrometry in Structural and Stereochemical Problems. CXLVIII. Electron Impact Induced Fragmentations of Some Cyclic Sulfites and Carbonates, *Tetrahedron 24*:2949–2967 (1968).

[Received October 16, 2003; accepted January 16, 2004]