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ORIGINAL PAPER

Conversion of Methyl Oleate to Branched-Chain Derivatives

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Abstract Studies were conducted in the synthetic conversion of oleic acid to mid-chain branched fatty acids. Methyl oleate was brominated in the allylic positions. Reaction of the allylic bromides with lithium dimethylcuprate gave primarily the desired branched-chain derivatives (93% of product mixture). The product had a significantly lower crystallization temperature in comparison with methyl oleate. Reaction of the allylic bromides with lithium di-*n*-butylcuprate or lithium di-*sec*-butylcuprate also gave branched-chain derivatives, but in this instance there was the complication of attack on the ester functionality in the fashion of a Grignard reagent. Details of the syntheses and the properties of the products (with emphasis on low-temperature properties) are discussed.

Keywords Allylic bromides · *Branched-chain fatty acids* · DSC · Low-temperature properties · Organocuprate reagents

Introduction

The use of vegetable oils as alternative diesel fuels (biodiesel) has been investigated for over a century. In the United States, soybean oil has received the most interest. However, neat vegetable oils pose a problem impairing their widespread use as biodiesel in that they cause engine deposits [1]. In an attempt to overcome this problem, biodiesel is typically obtained by the conversion of vegetable oils or animal fat to simple monoalkyl esters of fatty acids. These products, usually methyl or ethyl esters, can be used as alternative fuels or extenders in diesel engines. However, the relatively poor low-temperature properties of these biodiesel fuels present an obstacle to their continued development and commercialization [2, 3]. The conversion of vegetable oils and animal fats into esters of branched-chain alcohols, such as isopropyl or 2-butyl, has resulted in improved low-temperature properties, as demonstrated by their reduced crystallization onset temperatures [3–5].

Alkyl-branched fatty acids are widely distributed in nature, but are usually present in small quantities. Among the sources of branched-chain acids are animal fats and waxes and bacterial lipids [6, 7]. As an example, tuberculostearic acid (10-methyloctadecanoic acid) has been isolated from human tubercle bacilli and other bacterial lipids [7]. In addition, a number of branched-chained fatty acids have been identified as potential anticancer agents [8].

Simple monoalkyl esters or modified oils containing branched-chain fatty acids could have improved or superior low-temperature properties. Oleic acid and linoleic acid are the most abundant fatty acids of many vegetable oils, including cottonseed oil. As part of a project to develop new value-added industrial applications for cottonseed oil (such as biodiesel, fuel additives, and lubricants), studies were conducted in the synthetic conversion of oleic acid to branched fatty acids. In these studies, the model compound methyl oleate (**1**) was brominated in the allylic position and subsequently treated with cuprate reagents to produce branched-chain derivatives. Details of the syntheses and

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the properties of the products (with emphasis on low-temperature properties) are discussed.

Experimental Procedures

Materials

Methyl oleate (99%), *N*-bromosuccinimide (NBS, 99%), 2,2′-azobis (2-methylpropionitrile) [AIBN, 98%], methyllithium (1.6 M in diethyl ether), *n*-butyllithium (1.6 M in hexanes), *sec*-butyllithium (1.4 M in cyclohexane), silica gel (Merck, grade 9385, 230–400 mesh, 60 A), and diethyl ether (anhydrous, 99%+, ACS reagent) were purchased from Aldrich Chemical Company, Milwaukee, WI). Cuprous iodide (98%) was purchased from Alfa-Aesar (Ward Hill, MA). Calcium hydride (97%+) was purchased from Fluka (Milwaukee, WI). Diethyl ether was distilled from calcium hydride and stored over Type 4A molecular sieves under a nitrogen atmosphere.

Gas Chromatography/Mass Spectroscopy

A 1 μL aliquot of the sample was injected into a split/splitless injector (300 °C) on an Agilent 6890 Gas Chromatograph (Palo Alto, CA). The initial column pressure was held at 25 psi and a constant flow rate of 1.2 mL/min was maintained through the column using electronic pressure control (EPC). The oven temperature was held at 50 °C for 1 min, and then raised at a rate of 3 °C /min to 80 °C; the rate was changed to 10 °C /min and the oven temperature raised to 340 °C and held for 18 min for a total run time of 55 minutes. The GC was equipped with a 0.25 mm ID × 30 m column coated with a 0.5 μm film of 5% diphenyl/95% dimethylsiloxane capillary column (DB-5 MS, J&W Scientific). The effluent from the column was analyzed by an Agilent 5973 MSD employing electron ionization and operated in scan mode from *m/z* 40–550. Initial identification of known compounds was made by comparison with the 7th edition of the Wiley Mass Spectral Library.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed using a Mettler DSC 821e Thermo-analytical device. The experiment consisted of heating the samples (6 mg) from –100 to +50 °C at a rate of 10 °C/min followed by a cooling from +50 to –100 °C at the same rate. The cycle was then repeated, and the thermal transitions recorded. The second cooling scan was used to find the re-crystallization temperature, T_c. The second heating scan was used to find the onset and midpoint of glass transition temperature, T_g, and the melting temperature, T_m.

Nuclear Magnetic Resonance Spectroscopy (NMR)

Solution-state NMR spectra were recorded at 9.4 Tesla on a Varian Inova NMR Spectrometer, using a 5 mm broad-band probe and operating at 25 °C. The ^{1}H (proton) spectra, at 400 MHz, had a sweep-width of 6,000 Hz, were acquired with a 90° pulse angle and a 2.5 s relaxation delay, and were referenced to internal tetramethylsilane (TMS). The ^{13}C spectra, at 400 MHz, had a sweep-width of 30,000 Hz for ^{13}C, were acquired with a 45° pulse angle and a 2 second relaxation delay, and were referenced to the $CDCl_3$ peak, as the TMS concentration was too low. For compounds **4a** and **5a**, a fully edited DEPT (distortionless enhancement polarization transfer) experiment was run using the standard flip angles of 45, 90 and 135°, followed by mathematical manipulation to generate the CH, CH_2 and CH_3 spectra.

Allylic Bromination of Methyl Oleate

A solution of methyl oleate (5.24 g, 17.7 mmol), NBS (3.61 g, 20.3 mmol), and AIBN (66.7 mg, 0.41 mmol) in 50 ml of CCl_4 was heated at reflux under nitrogen for 2 h. After cooling, the precipitate was filtered and the solvent was removed in vacuo, giving 6.63 g of a mixture of allylic bromides **2** and **3** (Scheme 1). This material, owing to its instability, was used in subsequent reactions without further purification.

Reaction of Allylic Bromides with Lithium Dimethylcuprate

Lithium dimethylcuprate was prepared *in situ* by the addition of 32.6 mL (52.2 mmol) of methyllithium (1.6 M in diethyl ether) to 4.97 g (26.1 mmol) of cuprous iodide stirred in 50 mL of dry ether under nitrogen at –30 °C [9]. The resulting pale yellow solution was stirred for 0.5 h and a solution of 1.62 g (ca. 4.32 mmol) of allylic bromides (**2**, **3**) in 40 mL of ether was added. A yellow precipitate immediately formed. The reaction mixture was stirred at –20 °C for 1.5 h and at 0 °C for 2 h. The reaction was quenched with 150 mL of saturated ammonium chloride solution (pH 8). The aqueous and organic solutions were allowed to separate overnight. The supernatant ether layer was decanted and solids were filtered from the aqueous layer. The deep blue aqueous layer was extracted with 100 mL of ether. The combined ether layers were washed with 100 mL of water and 100 mL of brine and dried

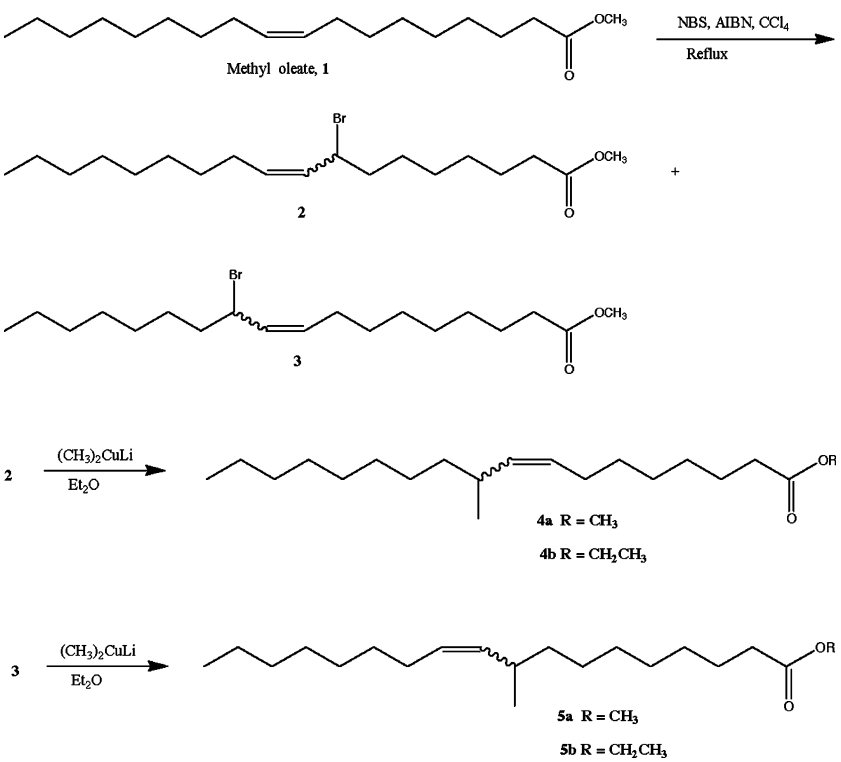
($MgSO_4$). Removal of solvent in vacuo afforded 1.31 g of product (**4** and **5**, Scheme 1) as a pale yellow oil.

Flash chromatography (silica gel, 2% ethyl acetate/hexanes eluant) [10] provided the analytical sample. GC/MS analysis of the purified material showed peaks with retention times of 28.80 min (81.4%) and 29.36 min (12.3%): mass spectra m/z (rel intensity); 28.80 min. retention time-310 (58), 279 (55), 194 (47), 180 (48), 179 (49), 166 (57), 153 (52), 152 (54). 151 (56), 140 (64), 139 (62), 125 (68), 123 (57), 111 (73), 97 (84), 83 (85), 81 (79), 69 (92), 67 (79), 55 (100), 43 (81), 41 (88); 29.36 min -324 (48), 279 (66), 278 (51), 185 (40), 171 (46), 157 (66), 139 (40), 125 (50), 111 (62), 97 (81), 83 (78), 69 (85), 67 (63), 55 (100), 43 (50), 41 (59). The following data were obtained for the major products **4a** and **5a** (Scheme 1): ^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3, CH_3), 0.96 (d, 3, CH_3), 1.63(m, 3, CH_2-$CH_2CO_2CH_3$), 1.99 (q, 2, CH_2CH=CHCH), 1.2–1.4 (m, 18, remaining 9 CH_2), 2.05 (m, 1, CH_2CH=CHC*H*), 2.33 (t, 2, $CH_2CO_2CH_3$), 3.69 (s, 3, OCH_3), 5.26 (dd, 1, CH_2CH=C*H*CH), and 5.36 (m, 1, CH_2C*H*=CHCH); ^{13}C NMR ($CDCl_3$) δ, 14.32, 21.15, 22.90, 25.19, 27.36, 27.48, 27.57, 28.92, 29.13, 29.16, 29.32, 29.33, 29.37, 29.39, 29.41, 29.48, 29.58, 29.60, 29.68, 29.70, 29.79, 29.84, 29.87, 29.93, 29.97, 30.01, 32.14, 32.69, 32.75, 32.80, 34.35, 36.91, 37.37, 37.42, 37.47, 51.62, 128.40, 128.51, 128.72, 128.77, 136.57, 136.63, 136.81, 136.90, 174.52.

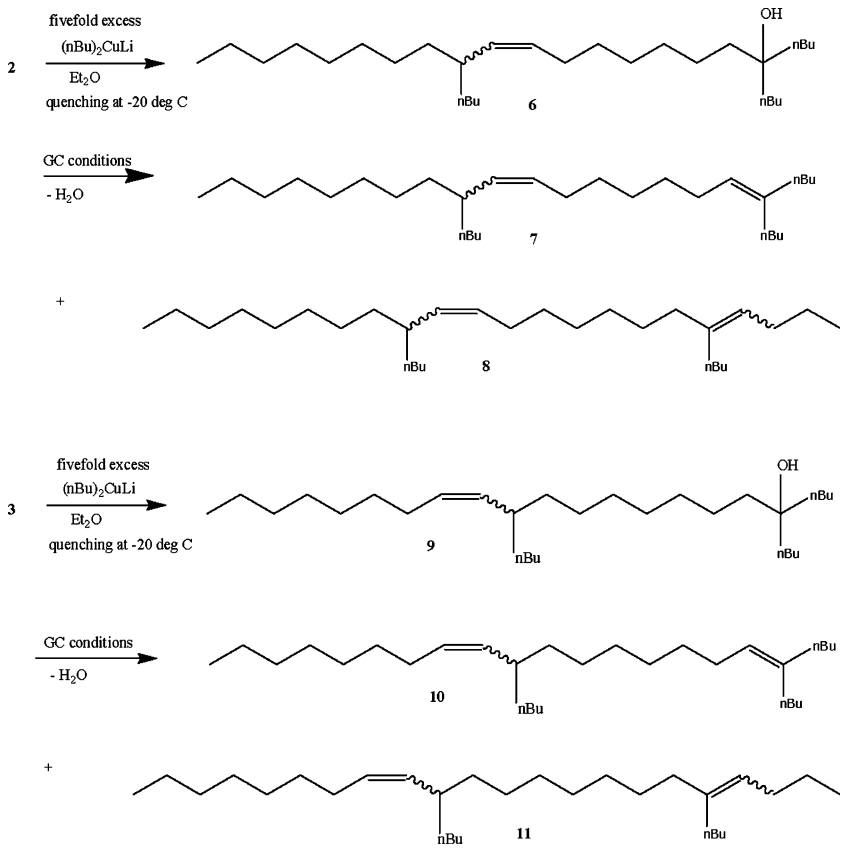
Reaction of Allylic Bromides with Lithium Di-*n*-Butylcuprate

Lithium di-*n*-butylcuprate was prepared in situ by the addition of 27.1 mL (43.4 mmol) of *n*-butyllithium (1.6 M in hexanes) to 4.13 g (21.7 mmol) of cuprous iodide stirred in 50 mL of dry ether under nitrogen at –30 °C [11]. The resulting reddish-black solution was cooled to –70 °C, and a solution of 1.63 g (*ca*. 4.34 mmol) of allylic bromides (**2**, **3**) in 40 mL of ether was added, maintaining the temperature below –60 °C. The reaction mixture was stirred at –70 °C for 1.5 h and at –20 °C for 0.5 h. The reaction was quenched with 40 mL of saturated ammonium chloride solution (pH 8), keeping the temperature below 0 °C. Thereafter, the entire reaction mixture was poured into 100 mL of saturated ammonium chloride solution (pH 8). The aqueous and organic solutions were allowed to separate overnight. The supernatant ether layer was decanted and solids were filtered from the aqueous layer. The deep blue aqueous layer was extracted with ether (2 × 100 mL). The combined ether layers were washed with 50 mL of ammonium chloride solution, 100 mL of water, and 100 mL of brine and dried ($MgSO_4$). Removal of solvent in vacuo afforded 1.69 g of product (predominantly **6** and **9**, Scheme 2) as a colorless oil.

A similar procedure was followed for the reaction of the allylic bromides (1.64 g, 4.36 mmol) with a fivefold excess



Scheme 1



Scheme 2

of lithium di-*sec*-butylcuprate, affording 1.58 g of crude product.

Flash chromatography (silica gel, 5% ethyl ether/hexanes eluant) provided the analytical sample of **6** and **9**: ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3, CH_3), 0.88 (t, 3, CH_3), 0.90 (t, 3, CH_3), 0.92 (t, 3, CH_3), 1.37–1.42 (m, 6, 3 C*H*$_2$–C–OH), 1.82 (br s, 1, O*H*), 1.96 (m, 3, C*H*$_2$CH=CHC*H*), 1.09–1.37 (m, 32, remaining 16 CH_2), 5.06 (dd, 1, CH_2CH=C*H*CH), and 5.29 (dt, 1, CH_2C*H*=CHCH); ^{13}C NMR ($CDCl_3$) δ, 14.34, 22.89, 22.92, 23.05, 23.57, 23.68, 23.71, 25.92, 27.50, 29.27, 29.31, 29.34, 29.41, 29.59, 29.60, 29.71, 29.75, 29.77, 29.88, 29.89, 29.94, 29.97, 29.99, 30.01, 30.38, 30.54, 32.14, 32.15, 32.81, 35.50, 35.51, 35.53, 35.80, 39.23, 39.54, 42.99, 43.00, 43.02, 74.60, 130.12, 130.17, 130.24, 130.27, 135.28, 135.31, 135.36, 135.40. GC/MS analysis of the purified material showed two overlapping peaks with retention times of 33.49 and 33.54 min (51.7 %) and two additional overlapping peaks with retention times of 34.58 and 34.79 min (48.3 %): mass spectra *m/z* (rel intensity); 33.49 min retention time-419 (48), 418 (100), 361 (22), 151 (45), 137 (42), 123 (58), 111 (49), 109 (65), 97 (75), 96 (54), 95 (71), 83 (73), 81 (65), 69 (80), 55 (80); 33.54 min - 419 (46), 418 (100), 361 (24), 151 (39), 137 (39), 123 (50), 111 (38), 109 (58), 97 (66), 96 (47), 95 (62), 83 (66), 81 (54), 69 (70), 55 (74); 34.58 min - 419 (46), 418 (89), 379 (55), 361 (34), 151 (44), 143 (100), 137 (41), 123 (56), 111 (49), 109 (61), 97 (70), 96 (48), 95 (69), 85 (54), 83 (76), 81 (63), 69 (81), 67 (57), 57 (60), 55 (80); 34.79 min - 419 (48), 418 (100), 379 (45), 361 (30), 151 (35), 143 (94), 137 (36), 123 (51), 111 (40), 109 (57), 97 (65), 96 (44), 95 (61), 85 (43), 83 (64), 81 (56), 69 (56), 67 (46), 57 (46), 55 (73).

Results and Discussion

GC/MS analysis of the product mixture obtained in reaction of allylic bromides **2** and **3** with lithium dimethylcuprate indicated the presence of 2.7% unreacted methyl oleate **1**, 93.0% of compounds with M^+ 310 (**4a** and **5a**, Scheme 1) and 2.7% of compounds with M^+ 324 (**4b** and **5b**, Scheme 1). The assignment of the structures **4a** and **5a** to the major products is based upon nucleophilic attack at the γ-carbon *via* the S_N2' mechanism [12]. The presence of the ethyl esters **4b** and **5b** was unexpected. GC/MS of the methyl oleate used as starting material showed no impurities. The analytical sample obtained after flash chromatography contained a substantially larger percentage of

ethyl esters (ca. 12%). Apparently, some transesterification took place under both reaction conditions and chromatographic conditions.

The proton NMR spectrum of the analytical sample of branched methyl derivatives of methyl oleate is shown in Fig. 2. The observed chemical shifts of the peaks are consistent with structures **4a** and **5a**. The spectrum showed no evidence of double bond migration. Peak assignments were made using the proton NMR spectrum of methyl oleate [13] as a guide. The chemical shifts (in ppm) for the peaks are as follows: a, 0.91; b, 0.96; c, 1.3–1.4; d, 1.63; e, 1.99; f, 2.05; g, 2.33; h, 3.69; i, 5.26; j, 5.36. The quartet centered at 4.15 ppm (corresponding to the CH_2 of an ethyl ester) confirms the presence of the minor products **4b** and **5b**. Based upon integration of the peaks at 4.15 ppm and 0.91 ppm, **4b** and **5b** represent *ca.* 6.7% of the product. This figure is considerably lower than the figure obtained from GC data and should be more accurate.

The configuration about the double bond in compounds **4a** and **5a** is not specified (Fig. 1). However, analysis of the ^{13}C NMR data indicates the *cis* configuration. There are two sets of four peaks in the olefinic region, the first set ranging from 128.40 to 128.77 ppm and the second set ranging from 136.57 to 136.90 ppm. Calculations using alkene shift parameters [15] provide values of 128.5 and 137.5 ppm for the *cis* alkene, in excellent agreement with the observed chemical shifts. The fact that there are eight olefinic chemical shifts instead of four may be attributed to the asymmetric center at the site of branching. The DEPT spectrum analysis allows for the following assignments: δ 14.32 (terminal CH_3); 21.15 (branch CH_3); 36.91 ($CH_2CH{=}CHCH$); 51.62 (OCH_3) (Fig. 2).

Lithium dialkylcuprates were selected for the introduction of branch chains since these reagents are reported to be unreactive toward esters under the conditions employed. The ester n-$C_4H_9CO_2CH_3$ was recovered (>85%) when

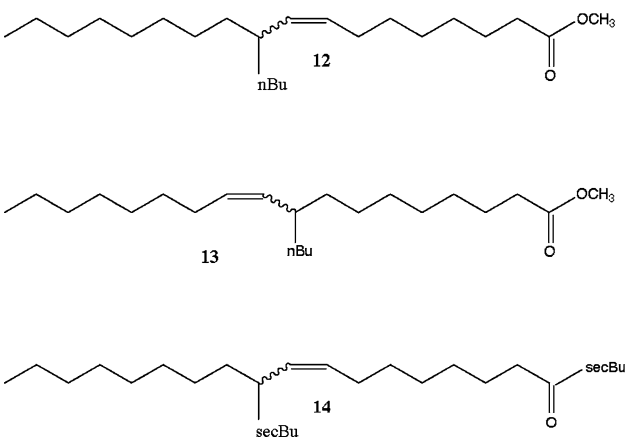


Fig. 1 Structures of compounds **12**, **13**, and **14**

treated with three equivalents of lithium dimethylcuprate at 18°C or three equivalents of lithium di-*n*-butylcuprate at –10°C. [14]. However, GC/MS analysis of the product mixture obtained in reaction of allylic bromides **2** and **3** with five equivalents of lithium di-*n*-butylcuprate indicated the absence of the expected products **12** and **13** (Figure 1). The major products had apparent M^+ of 362 (7.6%), 360 (15.0%) and 418 (71.6%). The most plausible structures for products with M^+ 418 are **7**, **8**, **10**, and **11** (Scheme 2). These structures are consistent with the expected S_N2' substitution of bromine and attack of the ester functionality in the fashion of a Grignard reagent to form tertiary alcohols followed by elimination of water. However, GC/MS and NMR studies of the purified analytical sample indicate that the compounds actually isolated are the tertiary alcohols **6** and **9**. GC/MS analysis showed two overlapping peaks with retention times of 33.49 and 33.54 min and two additional overlapping peaks with retention times of 34.58 and 34.79 min. The mass spectra of the first two eluted materials were essentially identical and consistent with the structures **7**, **8**, **10**, and **11**. However, the mass spectra of the last two eluted materials showed two additional prominent fragment ions (*m/z* 379 and *m/z* 143). The presence of these ions strongly suggests that the eluted compounds are the **6** and **9**. The peak at *m/z* 379 corresponds to loss of *n*-butyl from **6** or **9** (molecular weight 436). The peak at m/z 143 corresponds to the highly stable ion $[(n\mathrm{Bu})_2C{=}OH]^+$.

Analysis of the NMR spectra provides further confirmation of the structural assignments **6** and **9**. The ^1H NMR spectrums shows the presence of only one double bond and the complete absence of a methyl ester. In the ^{13}C NMR spectrum, the chemical shift at 74.60 ppm is highly indicative of a tertiary carbon atom bearing the hydroxyl group. Analysis of the ^{13}C NMR data indicates the configuration about the double bond in compounds **6** and **9** is *cis*. As was the case with **4a** and **5a**, there are two sets of 4 peaks in the olefinic region. The first set ranges from 130.12 to 130.27 ppm and the second set ranges from 135.28 to 135.40 ppm. Calculations using alkene shift parameters [15] provide values of 130.0 and 136.0 ppm for the cis alkene, in excellent agreement with the observed chemical shifts.

GC/MS analysis of the product mixture obtained in reaction of allylic bromides **2** and **3** with lithium di-*sec*-butylcuprate indicated major products with apparent M^+ of 360, 362, 378, and 418 (most abundant). The material with apparent M^+ 418 should be *sec*-butyl analogs of the tertiary alcohols **6** and **9**, as discussed above. A plausible structure (**14**) for one of the products with M^+ of 378 (resulting from S_N2' substitution of bromine and attack of the ester functionality by one equivalent of cuprate reagent) is shown in Fig. 1.

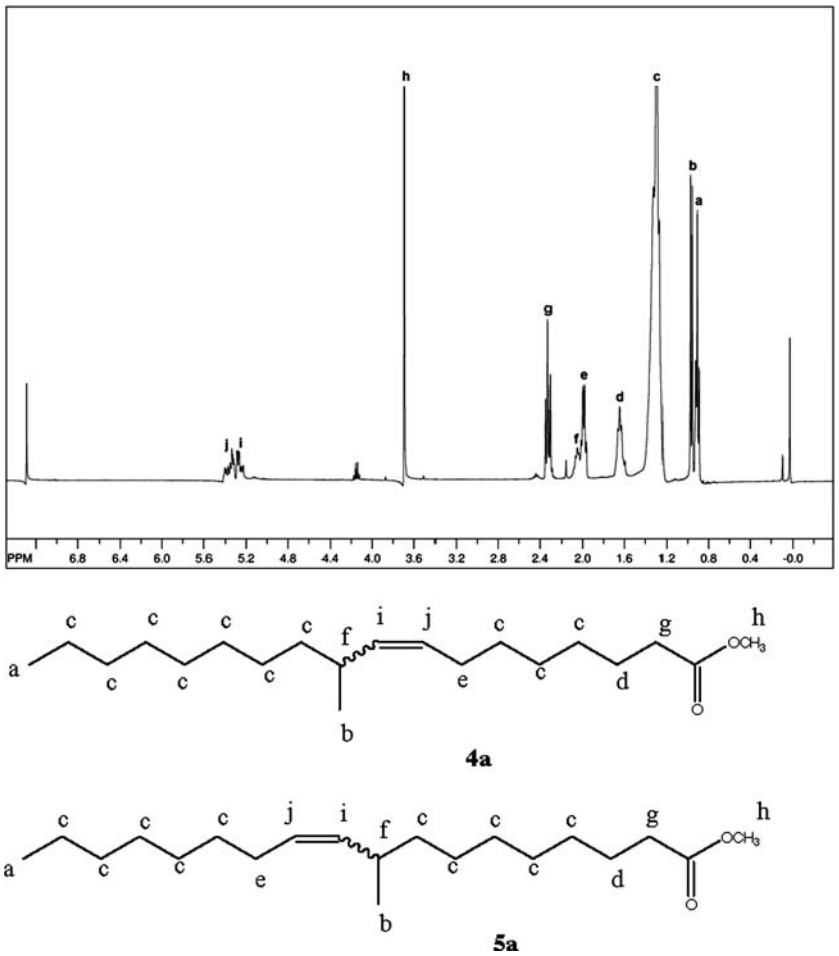


Fig. 2 Proton NMR of methyl derivatives **4a** and **5a**. Assignments of peaks to the corresponding protons are made in the structural diagrams

Table 1 DSC properties of products of reaction of allylic bromides **2**, **3**, and **4** with cuprate reagents R_2CuLi

Major Compound(s)	*R*	T_c °C	T_m °C	T_g °C
Methyl oleate **1**		–42.0, –44.5	–15.7	
4, 5	CH_3	–54.1, –87.2	–42.4, –74.5	
6, 9	*n*-Bu			–77.0 (onset)
				–73.3 (midpt.)
	sec-Bu			–81.9 (onset)
				–76.3 (midpt.)

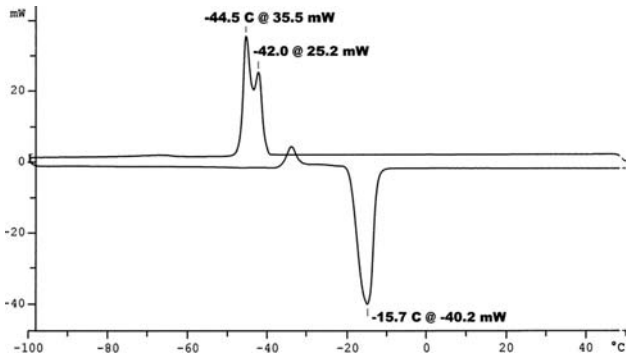


Fig. 3 DSC thermogram of methyl oleate. The lower scan is the heating curve. The upper scan is the cooling curve

DSC studies were conducted on the products of reactions of allylic bromides **2** and **3** with the three different cuprate reagents. The results are summarized in Table 1. A commercial sample of methyl oleate, used for comparison purposes, gave T_c maxima at –42.0 and –44.5 °C and a T_m of –15.7 °C (Fig. 3). In the DSC thermogram (Fig. 4) of the lithium dimethylcuprate products (93% **4a** and **5a**), the first of the two Tc maxima (–54.1 °C) was of the greatest magnitude and was substantially lower than the T_c of methyl oleate. The T_m minimum at –74.5 °C was of the greatest magnitude. The DSC thermogram of reaction products of lithium di-*n*-butylcuprate and **2** and **3** is shown in Fig. 5.

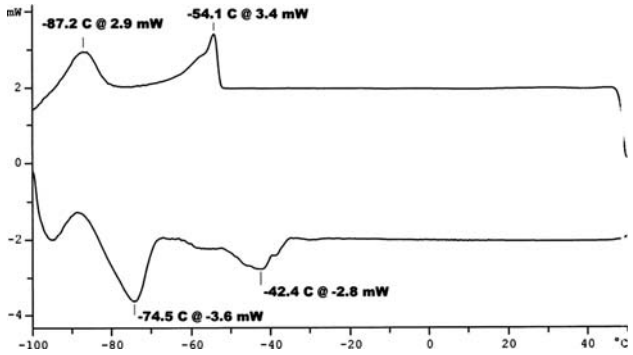


Fig. 4 DSC thermogram of methyl derivatives **4** and **5**. The lower scan is the heating curve. The upper scan is the cooling curve

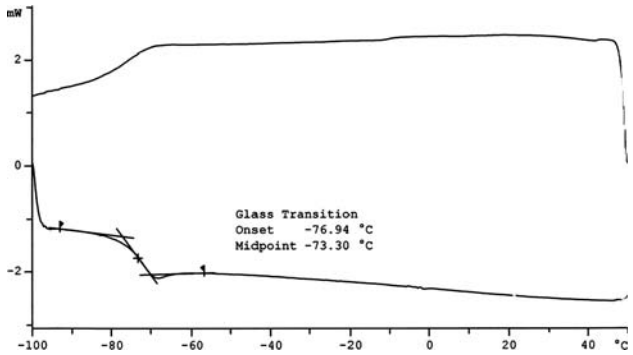


Fig. 5 DSC thermogram of reaction products of lithium di-*n*-butylcuprate and **2** and **3**. The lower scan is the heating curve. The upper scan is the cooling curve

As shown in Table 1, the *n*-butyl products (primarily the tertiary alcohols **6** and **9**) exhibited only a glass-transition temperature (–73.3 °C) with the more highly branched *sec*-butyl products giving slightly lower values (–76.3 °C).

The significantly lower re-crystallization temperature of branched-chain derivatives (**4a** and **5a**) of methyl oleate provides evidence that simple monoalkyl esters or modified oils containing branched-chain fatty acids could have improved or superior low-temperature properties as biodiesel fuel or fuel additives. Modification of reaction conditions (lower temperature, less organocuprate reagent) should provide other branched-chain derivatives such as the *n*-butyl derivatives **12** and **13**.

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References

1. Knothe G, Dunn RO, Bagby MO (1997) Biodiesel: the use of vegetable oils and their derivatives as alternative diesel fuels. In: ACS Symp. Ser. 666 (Fuels and Chemicals from Biomass). American Chemical Society, Washington, pp 172–208
2. Dunn RO (1999) Thermal analysis of alternative diesel fuels from vegetable oils. J Am Oil Chem Soc 76:109–115
3. Lee I, Johnson LA, Hammond EG (1995) Use of branched-Chain esters to reduce the crystallization temperature of biodiesel. Ibid 72:1155–1160
4. Foglia TA, Nelson LA, Dunn RO, Marmer WN (1997) Low-temperature properties of alkyl esters of tallow and grease. Ibid 74:951–955
5. Wu W-H, Foglia TA, Marmer WN, Dunn RO, Goering CE, Briggs TE (1998) Low-temperature property and engine performance evaluation of ethyl and isopropyl esters of tallow and grease. Ibid 75:1173–1178
6. Gunstone FD (1994) Fatty Acid Structure. In: Gunstone FD, Harwood JL, Padley FB (eds) The lipid handbook. Chapman & Hall, London, pp 11–12
7. Polgar N (1971) Natural alkyl-branched long-chain acids. Top lipid chem 2:207–246
8. Yang Z (2001) Anticancer effects of specific branched-chain fatty acids and related production process. US. Patent No. 6,214,875
9. Corey EJ, Posner GH (1967) Selective formation of carbon-carbon bonds between unlike groups using organocopper reagents. J Am Chem Soc 89:3911–3912
10. Still WC, Kahn M, Mitra A (1978) Rapid chromatographic techniques for preparative separation with moderate resolution. J Org Chem 43:2923–2925
11. Corey EJ, Posner GH (1968) Carbon-carbon bond formation by selective coupling of *n*-alkylcopper reagents with organic halides. J Am Chem Soc 90:5615–5616
12. van Tamelen EE, McCormick JP (1970) Synthesis of *Cecropia* Juvenile Hormone from *trans*, *trans*-Farnesol. Ibid 92:737–738
13. The Lipid Library (2006) ^{1}H-NMR spectroscopy of fatty acids with non-conjugated double bonds. http://www.lipidlibrary.co.uk./nmr/1NMRdbs/index.htm
14. Posner GH, Whitten CE, McFarland PE (1972) Organocopper chemistry. Halo-, cyano-, and carbonyl-substituted ketones from the corresponding acyl chlorides and organocopper reagents. J Am Chem Soc 94:5106–5108
15. Dorman DE, Jautelat M, Roberts JD (1971) Carbon-13 nuclear magnetic resonance spectroscopy. Quantitative correlations of the carbon chemical shifts of acyclic alkenes. J Org Chem 36:2757–2766