of 4 (0.50 g, 1.7 mmol), obtained from the preceding experiment, in methanol (10 mL) was added a solution of potassium carbonate (0.23 g, 1.7 mmol) in water (10 mL). After the reaction mixture was stirred for 10 min, the solvent was evaporated under reduced pressure to give a white solid residue. This was triturated with methylene chloride (50 mL × 3) and the organic solution was washed with water twice and dried (Na_2SO_4). The solvent was removed to obtain the β form of **5** as a white crystalline solid (0.43 g, 100%): mp 122–123 °C; ^{1}H NMR (60 MHz) ($CDCl_3$) δ 1.65 (s, 3 H, 2-CH_3), 3.12 (t, 2 H, J = 5.5 Hz, 4-CH_2), 4.08 (t, 1 H, J = 3.5 Hz, OH), 4.17–4.57 (m, 3 H, 5-CH_2 and methine CH), 7.07–7.73 (m, 5 H, ArH), 8.53 (s, 1 H, NH); IR (KBr) 3350 (OH), 3250 (NH), 1660 (C=O) cm^{-1}.

B. In the same way as in **A** the α form of **4** (0.3 g, 1 mmol) was hydrolyzed to give the α form of **5**, white crystalline solid (0.25 g, 97%): mp 133–135 °C; ^{1}H NMR (60 MHz) ($CDCl_3$) δ 1.75 (s, 3 H, 2-CH_3), 2.90–3.13 (m, 2 H, 4-CH_2), 4.03 (t, 1 H, J = 3.5 Hz, OH), 4.17–4.50 (m, 3 H, 5-CH_2 and methine CH), 7.10–7.70 (m, 5 H, ArH), 8.52 (s, 1 H, NH); IR (KBr) 3270 (OH and NH), 1650 (C=O) cm^{-1}. Anal. ($C_{12}H_{15}O_3NH$) C, H, N.

C. Likewise, a mixture of the α and β forms of **4** (6.21 g, 21 mmol) was hydrolyzed to obtain the corresponding mixture of **5** (5.22 g, 98%). These diastereomers could not be separated by chromatography due to identical flow rates.

Synthesis of 5,6-Dihydro-3-methyl-*N*-phenyl-1,4-oxathiin-2-carboxamide (2). A solution of β-hydroxy-1,3-oxathiolanes **5** as a diastereomeric mixture (0.2 g, 0.8 mmol) and PTSA (8 mg) in dry toluene (20 mL) was refluxed with a Dean–Stark water separator for 30 h. The reaction mixture was cooled, washed with water and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to give a light yellow oily residue (0.19 g), which was a 90:10 mixture of **2** and **1** as determined by ^{1}H NMR spectroscopy. These were separated by preparative TLC (Kiesel gel GF 254), using benzene as eluent. The first band (R_f 0.4) and the second band (R_f 0.2) were extracted with chloroform to obtain **2** (165 mg, 89%) and **1** (18 mg, 10%), respectively.

For **2**: mp 82.5–84 °C; ^{1}H NMR (60 MHz) ($CDCl_3$) δ 2.42 (s, 3 H, CH_3), 3.02–3.18 (m, 2 H, 5-CH_2), 4.25–4.40 (m, 2 H, 6-CH_2), 7.03–7.80 (m, 5 H, ArH), 8.47 (s, 1 H, NH); IR (KBr) 3300 (NH), 1650 (C=O) cm^{-1}; mass spectrum (70 eV), m/e (relative intensity) 235 (54.1, M^+), 143 (100, $M^+ - C_6H_5NH_2$), 115 (10.7, $M^+ - C_6H_5NHCO$). Anal. ($C_{12}H_{13}O_2NS$) C, H, N, S.

Independent Synthesis of Compound 2. A. Preparation of 2-Oxo-*N*-phenylbutanamide. To a stirred solution of 2-oxobutanoic acid (10.2 g, 0.1 mol) and aniline (18.2 mL, 0.2 mol) in methylene chloride (600 mL) at 0–5 °C was added a solution of dicyclohexylcarbodiimide (20.6 g, 0.1 mol) in methylene chloride (200 mL) dropwise over 3 h. Stirring was continued at ambient temperature for 16 h. The white solid precipitates were filtered off and the solution was washed with a 1 N HCl solution and then with water and dried (Na_2SO_4). The solvent was removed under reduced pressure to give a light yellow oily residue. This was chromatographed on a silica gel (Kiesel gel 60, 70–230 mesh) column using benzene–ethyl acetate (7:3) as eluent to obtain 2-oxo-*N*-phenylbutanamide (5.32 g, 30%); ^{1}H NMR (60 MHz) ($CDCl_3$) δ 1.15 (t, 3 H, J = 6.5 Hz, CH_3), 3.01 (q, 2 H, J = 6.5 Hz, CH_2), 7.00–7.83 (m, 5 H, ArH), 8.81 (s, 1 H, NH); IR (KBr) 3300 (NH), 1710 (C=O), 1670 (C=O) cm^{-1}.

B. Preparation of 3-Bromo-2-oxo-*N*-phenylbutanamide (11). To a stirred solution of 2-oxo-*N*-phenylbutanamide (177 mg, 1 mmol) in dry benzene (2 mL) was added a solution of bromine (26 mmL) in benzene (1 mL) at room temperature, and the reaction mixture was allowed to stir for 2 h. The solvent was evaporated under reduced pressure to give a yellow solid (256 mg). Crystallization from benzene gave **11** (220 mg, 86%) as light yellow plates: mp 109–111 °C; ^{1}H NMR (60 MHz) ($CDCl_3$) δ 1.88 (d, 3 H, J = 7 Hz, CH_3), 5.63 (q, 1 H, J = 7 Hz, CH), 7.10–7.90 (m, 5 H, ArH), 8.83 (s, 1 H, NH); IR (KBr) 3300 (NH), 1680 (C=O) cm^{-1}.

C. Preparation of 3-[(2-Hydroxyethyl)thio]-2-oxo-*N*-phenylbutanamide (9). To a stirred solution of 3-bromo-2-oxo-*N*-phenylbutanamide (**11**) (256 mg, 1 mmol) in benzene (2 mL) was added a solution of potassium hydroxide (67 mg), 2-mercaptoethanol (82 mg, 1 mmol) in methanol (0.1 mL). The reaction mixture was allowed to stir for 35 min and the solvent evaporated under reduced pressure. The residue was dissolved in methylene chloride, washed with water, and dried (Na_2SO_4). On removing the solvent there was obtained white foamy solid (0.24 g). Crystallization from toluene gave a white solid (0.14 g, 55%) as a diastereomeric mixture of **9** in cyclic form **10** as shown by ^{1}H NMR spectroscopy: mp 77–85 °C; ^{1}H NMR (60 MHz) ($CDCl_3$) δ 1.12 (d, 2.1 H^a, J = 7 Hz, CH_3), 1.50 (d, 0.9 H^b, J = 7 Hz, CH_3), 1.87–4.47 (m, 5 H, 4-CH_2, 5-CH_2, and 3-CH), 4.92 (s, 0.7 H^a, OH), 4.98 (s, 0.3 H^b, OH), 7.00–7.73 (m, 5 H, ArH), 8.53 (s, 1 H, NH); IR (KBr) 3350 (OH), 3200 (NH), 1760 (C=O) cm^{-1} [a/b = 7/3 = diastereomeric ratio].

D. Preparation of 5,6-Dihydro-3-methyl-*N*-phenyl-1,4-oxathiin-2-carboxamide (2). A solution of 3-[(2-hydroxyethyl)thio]-2-oxo-*N*-phenylbutanamide (**9**) (0.24 g, 0.95 mmol) and PTSA (9 mg) in dry toluene (20 mL) was refluxed with a Dean–Stark water separator for 2 h. The toluene solution was cooled, washed with sodium bicarbonate solution and with water, and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to give a yellow solid (0.235 g). Crystallization from ethyl acetate–petroleum ether gave colorless short needles (0.17 g, 76%). This compound had identical ^{1}H NMR and IR spectra with those of the compound **2** obtained by the previous method.

Registry No. **1**, 5234-68-4; **2**, 69892-02-0; **3**, 119878-79-4; α-**4**, 779878-82-9; β-**4**, 779878-80-7; α-**5**, 779878-83-0; β-**5**, 119878-81-8; **9**, 119878-84-1; **10** (isomer 1), 119878-85-2; **10** (isomer 2), 119878-87-4; **11**, 779878-86-3; α-chloroacetoacetanilide, 119878-78-3; 2-mercaptoethanol, 60-24-2; 2-oxobutanoic acid, 600-18-0; aniline, 62-53-3; 2-oxo-*N*-phenylbutanamide, 72681-68-6.

S-Alkylation of Camphorthione with Diazo Esters

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Diazo compounds react with thiones to afford thiadiazolines, which can be converted by thermal "two-fold extrusion" reactions to alkenes.[2] Intermediate in this sequence is an episulfide. The method was developed as a route to highly hindered alkenes (e.g. **3a**)[2d] (Scheme I) and has not been used frequently in synthetic pathways.

Refluxing a THF solution of **1** and **2b** led to the slow disappearance of the starting materials and the formation of a single new product (63%) whose molecular weight corresponded to $C_{14}H_{22}O_2S$. The presence of a vinyl proton (δ = 5.6) in the NMR spectrum and subsequent transformations clearly establish the structure of this product to be **5a**,[3] which was better prepared by the potassium *tert*-butoxide mediated alkylation of **1** with ethyl bromoacetate[3] (Scheme II) (75%). In a similar way, compounds **5b** and **5c** were prepared in 62 and 69% yields, respectively. The NMR spectra showed these to be the expected 1:1 mixture of diastereomers.

Alkaline hydrolysis of **5a** followed by acidification of an aqueous solution of the potassium salt led to a new compound (80%) whose spectroscopic data (IR 1775 cm^{-1}, FIMS = 226) identified it as **6a**. Both the 300-MHz ^{1}H NMR and the 75-MHz ^{13}C NMR spectra establish this structure and confirm the presence of both stereoisomers

(1) Holder NSERC undergraduate summer research award, 1986.

(2) (a) Barton, D. H. R.; Willis, B. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1225. (b) Barton, D. H. R.; Smith, E. H.; Willis, B. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1226. (c) Barton, D. H. R.; Willis, B. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 305. (d) Barton, D. H. R.; Guziec, F. S.; Shahak, I. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1794.

(3) Veenstra, G. E.; Zwanenburg, B. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 37.

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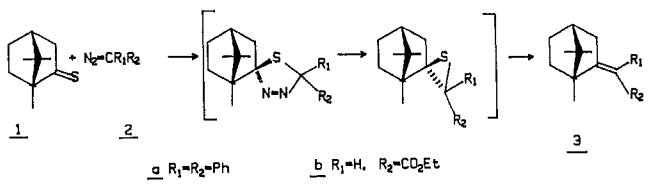
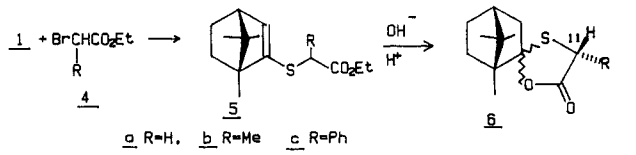
Scheme I



Scheme II



in a 4:1 ratio. The C-11 protons of the major isomer appeared as a singlet superimposed on those of the minor isomer, which appeared as an AB quartet. NOE experiments failed to distinguish between the two stereoisomers. On the basis of the known proclivity of bornylene derivatives to be attacked from the endo face, we assign the major diastereomer the structure with the exo sulfur atom. Chromatographic separation of the diastereomers was not achieved. Gas chromatographic analysis of the mixture resulted in two peaks of varying relative sizes. GC/MS analysis indicated that the earlier peak possessed the formula $C_{11}H_{18}S$ and probably arises from the known[4] pyrolysis of the oxathiolanone system to the episulfide. Hydrolysis of **6a** provided camphor and mercaptoacetic acid.

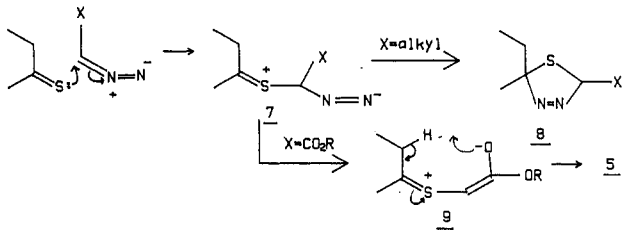
Models suggest that a substituted oxathiolanone whose substituent is syn to the C-10 methyl group of camphor should be significantly more hindered than the anti isomer. Thus it was expected that the diastereomeric mixtures of **5b** and **5c** would afford only two of the possible four stereoisomers of **6**. In the event, cyclization of **5b** afforded **6b** (53%) whose NMR clearly confirmed the presence of only two diastereomers. Although **5b** was composed of equal amounts of two diastereomers, the NMR spectra of **6b** indicated an unequal amount of the two cyclization products. Presumably this is due to unequal cyclization efficiency. Separation of these stereoisomers has not been achieved. Hydrolysis of **5c** led to a low yield of a mixture of compounds, but the ^1H NMR spectrum indicated the presence of only two stereoisomers of **6c**.

The reaction found between **1** and **2a** is apparently a previously unreported type. Since **1** has been shown to form thiadiazolines with other simple diazo compounds, the difference in the present case must be caused by the ester group. To rationalize these results, the process shown in Scheme III is proposed. Attack of the nucleophilic sulfur atom on the diazo compound leads to **7**. In the case where X is not a strong electron-attracting group, collapse of **7** to the thiadiazoline **8** occurs. However, if X = COOR, loss of N_2 leads to the formation of the ester enolate **9**, which is perfectly arranged to collapse to the observed product even though this thione is considerably less acidic than other enolizable thiones due to the strained bicyclo[2.2.1]heptane system.[5]

Experimental Section

Unless otherwise noted, infrared spectra were run as neat liquids and only the four most intense peaks are reported. The NMR spectra were run at 300 MHz for ^1H and 75 MHz for ^{13}C. Values in brackets are for the minor diastereomer. Gas chromatographic

Scheme III



analyses were performed with use of a 1.5 ft × $^1/_8$ in. column packed with 5% OV-101 on Chromosorb W (column A) or a 8 ft × $^1/_4$ in. column packed with 20% SE-30 on Chromosorb W (column B). Mass spectra were run in the electron impact (EI) or field ionization (FI) modes. Solvents were removed under reduced pressure, and the drying agent used was anhydrous magnesium sulfate. Column chromatography utilized silica gel 60. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Preparation of Compound 5. (a) Reaction of Ethyl Diazoacetate with Camphor Thione. A solution of 8.00 g (70 mmol) of camphor thione (**1**)[6] and 12.0 g (71 mmol) of ethyl diazoacetate[7] in 50 mL of dry THF was refluxed under a nitrogen atmosphere for 26 h at which point gas chromatographic analysis indicated that about 50% conversion of the starting materials had taken place. Refluxing for a further 90 h completed the reaction. Evaporation and chromatographic purification (petroleum ether eluant) afforded 12.0 g (64%) of a clear oil, which was identical in all respects with the product obtained by method b.

(b) S-Alkylation of 1 with Ethyl Bromoacetate.[3] The literature procedure[3] was followed to afford a 75% yield of **5a**: IR 3058, 1738, 1563, 1268, 1140 cm^{-1}; ^1H NMR δ 5.58 (d, 1 H), 4.20 (dq, 2 H), 3.42 (AB q, 2 H), 2.38 (m, 1 H), 1.89 (m, 2 H), 1.49 (m, 1 H), 1.30 (t, 3 H), 1.15–0.9 (m, 2 H), 0.98 (s, 3 H), 0.82 (s, 3 H), 0.79 (s, 3 H); ^{13}C NMR δ 169.5, 142.8, 125.9, 61.5, 56.6, 56.3, 52.2, 33.9, 31.5, 26.4, 19.6, 19.4, 14.1, 11.1.

Alkylation of 1 with Ethyl 2-Bromopropionate. In the same manner as described for the preparation of **5a**, thione **1** was alkylated with ethyl 2-bromopropionate to afford a 62% yield of **5b** as a 1:1 mixture of diastereomers: ^1H NMR δ 5.90 (s, 1 H) [5.88 (s, 1 H)], 4.32 (m, 2 H), 3.72 (q, 1 H, J = 7.1 Hz) [3.66 (q, 1 H, J = 7.2 Hz)], 2.35 (t, 1 H, J = 3.4 Hz), 1.87 (m, 1 H), 1.51 (d, 3 H, J = 7.1 Hz) [1.50 (d, 3 H, J = 7.1 Hz)], 1.28 (t, 3 H, J = 7.0 Hz) [1.26 (t, 3 H, J = 7.0 Hz)], 1.00 (s, 3 H) [0.99 (s, 3 H)], 0.82 (s, 3 H) [0.81 (s, 3 H)], 0.77 (s, 3 H); ^{13}C NMR δ 142.0 [141.7], 128.3 [127.5], 61.3 [61.2], 56.7 [56.6], 55.7, 52.3 [52.2], 42.4 [42.1], 31.5 [31.3], 26.3, 19.6 [19.4], 17.5 [17.2], 14.1, 11.2. Anal. Calcd for $C_{15}H_{24}O_2S$: C, 67.12; H, 9.01. Found: C, 66.88; H, 8.89.

Hydrolysis and Cyclization of 5a. To a solution of 6.0 g (0.024 mol) of **5a** in 20 mL of ethanol was added an ethanolic solution of 1.33 g (0.024 mol) of KOH, and the solution was stirred at ambient temperature overnight. The solvent was evaporated, and the solid was dried under vacuum. The solid was dissolved in water (25 mL) at −10 °C and stirred for 10 min, and then 10% hydrochloric acid was added dropwise with stirring until the pH fell to ca. 6.5. A thick oil precipitated while the acidification was in progress, and ether (30 mL) was added to facilitate the stirring. The solution was stirred for 10 min after the acid addition was complete, the layers were separated, and the aqueous layer was extracted with ether. The combined ethereal extracts were washed with water, dried, and evaporated to give 2.43 g of an orange-tinted oil, which was purified by column chromatography with 8:1:1 petroleum ether–dichloromethane–ether as eluant. The gas chromatograph of the product (on column B) showed two widely separated peaks of equal intensity, which was not compatible with the other spectroscopic data. GC/MS analysis of the product showed that the two peaks were due to materials with the molecular weights 182 and 226, which is consistent with the episulfide derived by loss of CO_2 from **6a**, and **6a** itself. The NMR data indicated the presence of two diastereomers in a ratio of 4:1: ^1H

(4) Cameron, T. B.; Pinnick, H. W. *J. Am. Chem. Soc.* **1980**, *102*, 744.
(5) Paquer, D.; Vialle, J. *Bull. Soc. Chim. Fr.* **1969**, 3595.
(6) McIntosh, J. M.; Mishra, P. *Can. J. Chem.* **1985**, *64*, 726.
(7) Searle, N. E. *Org. React.* **1963**, *3*, 424.

NMR δ 3.67 (s, 2 H) [3.64 (AB q, 2 H, J = 16.6 Hz)], 2.43 (dt, 1 H, J = 4.2, 15.0 Hz) [2.61 (dt, 1 H, J = 4.2, 15.0 Hz), 2.12–1.10 (m, 6 H), 1.02 (s, 3 H) [1.07 (s, 3 H)], 0.98 (s, 3 H) [0.92 (s, 3 H)], 0.90 (s, 3 H); ^{13}C NMR δ 172.4, 101.0, [101.6], 55.6 [54.6], 49.4 [49.0], 47.7, 45.6 [45.1], 33.3 [31.9], 29.6 [31.6], 26.5, 20.5, 20.3 [21.0], 11.6 [9.8]. Anal. Calcd for $C_{12}H_{18}O_2S$: C, 63.67; H, 8.01. Found: C, 63.74; H, 7.91.

Hydrolysis and Cyclization of 5b. In exactly the same manner as described above for **5a**, ester **5b** was converted to **6b** (53%). Gas chromatographic analysis of (column B) **6b** again showed two peaks. The NMR spectra clearly indicated the presence of two diastereomers in a ratio of 3:2: ^{1}H NMR δ 4.10 (q, 1 H, J = 7.3 Hz) [3.95 (q, 1 H, J = 7.0 Hz)], 2.65–1.60 (m, 7 H), 1.54 (d, 3 H, J = 6.9 Hz) [1.55 (d, 3 H, J = 7.0 Hz)], 0.97 (s, 3 H) [1.04 (s, 3 H)], 0.93 (s, 3 H) [0.99 (s, 3 H)], 0.91 (s, 3 H) [0.90 (s, 3 H)]. Anal. Calcd for $C_{13}H_{20}O_2S$: C, 64.96; H, 8.38. Found: C, 64.47; H, 8.26.

Preparation and Hydrolysis of 5c. In the same manner as described for the preparation of **5a**, thione 1 was alkylated with ethyl 2-bromophenylacetate to afford, after chromatography (20% ether in petroleum ether as eluant), a 62% yield of **5c** as a 1:1 mixture of diastereomers. The major impurity was diethyl 2,3-diphenylfumarate: ^{1}H NMR δ 7.6–7.1 (m, 5 H), 5.60 (dd, 1 H, J = 16.3, 3.3 Hz), 4.84 (d, 1 H, J = 19.6 Hz), 3.70 (m, 2 H), 2.41 (m, 1 H), 1.90–0.65 (m, 13 H).

Hydrolysis of **5c** according to the method outlined for **5a** and **5b** led to a mixture of compounds. The NMR of this mixture showed only two absorptions in the region of 5.0–6.0. Therefore it can be stated that only two of the four possible stereoisomers of **6c** were formed.

Acknowledgment. The financial assistance of the Natural Sciences and Engineering Research Council of Canada in the form of operating grants (to J.M.M.), a summer research grant (to P.A.S.), and equipment grants for the purchase of the NMR instrumentation made this work possible and is most gratefully acknowledged.

Registry No. 1, 53402-10-1; **2b**, 623-73-4; **4a**, 105-36-2; (±)-**4b**, 41978-69-2; (±)-**4c**, 2216-90-2; **5a**, 59056-16-5; **5b** (isomer 1), 119593-80-5; **5b** (isomer 2), 119717-06-5; **5c** (isomer 1), 119593-83-8; **5c** (isomer 2), 119677-24-6; **6a** (isomer 1), 119593-81-6; **6a** (isomer 2), 119677-22-4; **6b** (isomer 1), 119593-82-7; **6b** (isomer 2), 119677-23-5; **6c** (isomer 1), 119593-84-9; **6c** (isomer 2), 119677-25-7.

Synthesis of Pelargonic (Nonanoic) and Margaric (Heptadecanoic) Acid Methyl Esters from 1,3-Butadiene[1]

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Introduction

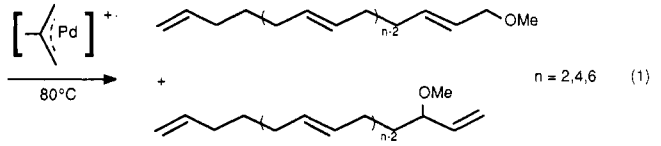
Fatty acids and their derivatives (esters, alcohols, amines) are important chemicals which mostly originate from natural oil and fats except for fatty alcohols which are produced synthetically.[2]

Synthetic fatty acids are available by ethylene oligomerization (Alfen[3] and Shop[4] processes) followed by various oxo processes (hydroformylation, hydrocarbonylation, ...).[5] These methods afford a distribution of linear fatty acids with odd carbon numbers which are often contaminated by less valuable regioisomers.

The preparation of a specific linear carboxylic acid can be achieved by applying the above-mentioned oxo methods to a particular olefin[5,6] and by various chemical methods,[7] the most valuable of which being the oxidative cleavage of the carbon–carbon double bond of a terminal olefin by neutral permanganate under phase-transfer conditions.[8] However, these methods require the synthesis or the separation of a given starting olefin.

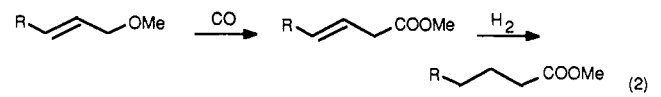
We report here an alternative synthesis, based on 1,3-butadiene, of two useful linear carboxylic esters and hence carboxylic acids, namely, pelargonic and margaric acid methyl esters, through a telomerization–carbonylation–hydrogenation sequence.

We previously described that mixtures of 1,3-butadiene and methanol can be easily transformed, with the aid of a cationic palladium catalyst, to telomers with an even number of butadiene units, with predominant formation of C_8 (n = 2; 20%) and C_{16} (n = 4; 34%) telomers (eq 1).[9]



From the reaction mixture, we were able to separate a C_8 fraction which contained 1-methoxyocta-2,7-diene (**1**) (90%) and 3-methoxyocta-1,7-diene (**2**) (10%) and a C_{16} fraction which consisted of 1-methoxyhexadecatetraene **3** (8%), 3-methoxyhexadeca-1,6,10,15-tetraene (**4**) (87%), and a hexadecapentaene (5%) (see Experimental Section).

We therefore envisioned that the carbonylation of these allylic ethers, followed by a hydrogenation step, could be a simple way to produce the corresponding saturated esters (eq 2). Carbonylation of allylic derivatives can be performed by using cobalt,[10] iron,[10] rhodium,[11,12] nickel,[10,13–15] platinum,[11,16] and mainly palladium[11,17–28] catalysts and has



(1) Part 1 of the series Carbonylation of Organic Allyl Moieties.
(2) *Kirk-Othmer Concise Encyclopedia of Chemical Technology*; Grayson, M., Ed.; Wiley: New York, 1985; pp 52–55 and 217–220. Hofmann, P.; Kosswig, K.; Schaefer, W. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 330. Hofmann, P.; Müller, W. H. E. *Hydrocarbon Process.* **1981**, *60*, 151.
(3) Weissermerl, K.; Harpe, H. J. *Chimie Organique Industrielle*; Masson: Paris, 1981; pp 68–76.
(4) Freitas, E. R.; Gum, C. R. *Chem. Eng. Prog.* **1979**, *75*, 73. Lutz, E. F. *J. Chem. Educ.* **1986**, *63*, 202.
(5) Cornils, B. *New Synthesis with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: New York, 1980; p 1. Müllen, A. *Ibid*, p 243.
(6) Waller, F. J. *Catalytic Conversion of Synthesis Gas and Alcohols to Chemicals*; Herman, R. G., Ed.; Plenum: New York, 1988; pp 193–202. Knifton, J. F. *J. Am. Oil Chem. Soc.* **1978**, *55*, 496. Protchenko, A. V.; Kron, T. E.; Karpyuk, A. D.; Petrov, E. S.; Tsvetkov, E. N.; Beletskaya, I. P. *Zh. Obshch. Khim.* **1986**, *56*, 90.
(7) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 1157.
(8) Lee, D. G.; Shannon, E. L.; Chang, V. S. *Org. Synth.* **1981**, *60*, 11.
(9) Grenouillet, P.; Neibecker, D.; Poirier, J.; Tkatchenko, I. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 767.
(10) Hanes, R. M.; Baugh, W. D. U.S. Patent 4 622 416, 1986.
(11) Knifton, J. F. *J. Organomet. Chem.* **1980**, *188*, 220.
(12) Murahashi, S.-I.; Imada, Y. *Chem. Lett.* **1985**, 1477.
(13) Cassar, L.; Chiusoli, G. P.; Guerrieri, F. *Synthesis* **1973**, 509.
(14) Foa, M.; Cassar, L. *Gazz. Chim. Ital.* **1979**, *109*, 619.
(15) Foo, J.; Alper, H. *Organometallics* **1985**, *4*, 1775.
(16) Parshall, G. W. *Z. Naturforsch.* **1963**, *18B*, 772.
(17) Tsuji, J.; Kiji, J.; Imamura, S.; Morikawa, M. *J. Am. Chem. Soc.* **1964**, *86*, 4350.
(18) Dent, W. T.; Long, R.; Whitfield, G. H. *J. Chem. Soc.* **1964**, 1588.
(19) Medema, D.; Van Helden, R.; Kohll, C. F. *Inorg. Chim. Acta* **1969**, *3*, 255.
(20) Imamura, S.; Tsuji, J. *Tetrahedron* **1969**, *25*, 4187.

0022-3263/89/1954-2459$01.50/0