Geminal Hydroxymethyl Compounds from 9(10)-Formylstearic Acid[1]

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ABSTRACT AND SUMMARY

9(10)-Formylstearic acid and methyl 9(10)-formylstearate reacted with formaldehyde in basic methanolic or aqueous medium to undergo the Tollens condensation, followed by a crossed Cannizzaro reaction to give 9,9(10,10)-bis(hydroxymethyl)-octadecanoic acid in essentially quantitative yield. This 2,2-disubstituted-1,3-propanediol has been esterified on the carboxyl group and the hydroxymethyl groups have been acetylated and acetalated with acetone to give a series of stable liquids boiling at ca. 200 C/0.005 mm and freezing at <-70 C.

INTRODUCTION

Reaction of formaldehyde with aliphatic aldehydes to form (hydroxymethyl)-aldehydes is the well-known Tollens condensation (1). All hydrogens *alpha* to the aldehyde function are replaced by hydroxymethyl groups. Under appropriate conditions, this reaction is followed by a crossed Cannizzaro reaction in which the aldehyde is reduced to an alcohol (2). This process is used commercially for the production of pentaerythritol (3). At the Northern Regional Research Center, these reactions have been applied to hexanal and nonanal to obtain the respective triols in high yield (4). The availability of 9(10)-formylstearic acid (FSA) and methyl 9(10)-formylstearate (MFS) by the selective hydroformylation of oleic acid and methyl oleate (5) furnished an opportunity to exploit the Tollens-Cannizzaro reactions for preparation of a novel 2,2-disubstituted-1,3-propanediol (2). We are here reporting the successful preparation of 9,9(10,10)-bis(hydroxymethyl)-octadecanoic acid (**1**) and several of its ester and acetal derivatives.

EXPERIMENTAL PROCEDURES

FSA and MFS were prepared by selective hydroformylation of oleic acid and methyl oleate, respectively (5).

Gas liquid chromatographic (GLC) data were obtained with a Hewlett-Packard Model 5700A chromatograph equipped with a hydrogen flame detector. The chromatograph was operated with a 6 ft x 1/8 in. stainless-steel column loaded with 10% OV-101 on 100-120 mesh HP Chromosorb W (Supelco, Inc., Bellefonte, PA). All runs were isothermal. Bis(hydroxymethyl)octadecanoic acid, its methyl and ethyl esters and their acetal and acetyl derivatives were analyzed at 240 C, the butyl ester series at 250 C, and the 2-ethylhexyl ester series at 260 C.

Samples for analysis (30-50 mg, ca. 150 mg for 2-ethylhexyl esters) were silylated (6) with 0.5 ml *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, Regis Chemical Company, Morton Grove, IL) at 160 C in 19 x 65 mm vials equipped with Sn-foil caps for 10 min. Water (10 μl) was added before silylation to samples of bis(hydroxymethyl)-octadecanoic esters. After cooling to room temperature, 0.2 μl (0.4 μl for 2-ethylhexyl esters) of silylation solution was injected. Samples not requiring silylation were dissolved in ether. FSA was esterified with diazomethane for analysis.

The mp were determined with a DuPont 940 thermomechanical analyzer by the method previously described (7).

Table I lists compounds prepared and their physical properties. The following experimental procedures for **1**, **2a**, **3**, **4a**, **4b**, and **5c** are exemplary of those used for corresponding compounds in the Table. Samples for characterization of **1**, its alkyl esters (**2**), and its acetone acetal (**3**) were synthesized by special procedures, given following the six preparative examples.

9,9(10,10)-Bis(hydroxymethyl) octadecanoic acid (1)

In methanol: An unstoppered 5000-ml 3-necked flask with a thermometer inserted through one neck was placed in an ice bath on a magnetic stirrer. A solution of 120 g (3 moles) sodium hydroxide in 500 ml water was stirred and cooled to about 2 C. Formaldehyde solution (225 g, 37.4%; 84.2 g, 2.8 moles formaldehyde) was added by means of an addition funnel. Addition was regulated to maintain a temperature less than 10 C and required 37 min. A solution of 477 g FSA (72.0%; 343 g, 1.1 moles) in methanol (total volume 1800 ml) was then added in the same manner over 2 hr and 55 min. The ice bath was removed after addition and the reaction mixture stirred overnight at room temperature. The mixture was then chilled to about 10 C and filtered to remove insoluble sodium stearate. The filter cake was washed with methanol and air dried (41.6 g). The filtrate was concentrated to about 1500 ml on the rotary evaporator, diluted with 500 ml water, acidified with 500 ml 25% sulfuric acid, and extracted with 2 x 1000 ml diethyl ether. The combined ether extracts were washed with 4 x 500 ml water, filtered, and dried over magnesium sulfate. After drying, the solution was filtered and the filtrate stripped on the rotary evaporator to leave 441 g of viscous liquid containing 79.9% **1** by GLC.

In water: The same procedure was followed except that 100 g FSA (92.3%; 92.3 g, 0.3 mole) was dissolved in 400 ml water containing 14 g (0.35 mole) sodium hydroxide. After addition, it was necessary to add 100 ml water to the reaction mixture to facilitate stirring. The product weighed 104 g and contained 95.9% **1**.

From MFS: A solution of 198 g MFS (97.6%; 193 g, 0.59 mole) in methanol (total volume 1000 ml) was used in the same procedure. This gave 202 g of product, 98.3% **1**.

Methyl 9,9(10,10)-Bis(hydroxymethyl)octadecanoate (2a)

A mixture of 141 g **1** (98%; 138 g, 0.4 mole), 500 ml methanol, and 1 ml concentrated sulfuric acid was heated to reflux. A sample taken after 1 hr showed that esterification was complete. The reaction mixture was cooled, 9 ml of 10% sodium hydroxide solution was added, and the solution stripped on the rotary evaporator. The residue was dissolved in 500 ml ether, washed with 4 x 250 ml water, filtered, and dried over magnesium sulfate. Filtration and evaporation left 147 g of liquid, 96.6% **2a** by GLC.

9,9(10,10)-Bis(hydroxymethyloctadecanoic Acid Acetone Acetal (3)[2]

A solution of 110 g **1** (82%; 90.2 g, 0.26 mole), 500 ml

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[1] Presented at the Symposium on "Industrial Uses of Fats and Oils," AOCS meeting, April, 1976, New Orleans.

[2] Ketal is no longer a recognized name: Fletcher, J.H., O.C. Dermer, and R.B. Fox, "Nomenclature of Organic Compounds," American Chemical Society, Washington, DC, 1974, p. 229.

TABLE I

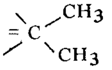
Properties of $CH_3(CH_2)_y\,C(CH_2\,OR')_2\,(CH_2)_x\,CO_2R$[a,b]

Cpd.	R	R'	GLC Purity (%)	mp, °C	bp, °C[c]	$n^{20}D$
1	H	H	99.6	−30.1	–	1.4767
2a	CH_3		99.8	−56.1	–	1.4688
2b	C_2H_5		100	−65.2	–	1.4656
2c	1-C_4H_9		100	−64.7	–	1.4656
2d	2-$(C_2H_5)C_6H_{12}$		97.8	−71.6	–	1.4663
3	H	1/2 C_3H_6[d]	100	−47.0	–	1.4663
4a	CH_3		100	−78.0	183	1.4590
4b	C_2H_5		99.6	−94.5	204	1.4572
4c	1-C_4H_9		100	−80.3	205	1.4580
4d	2-$(C_2H_5)C_6H_{12}$		97.8	−90.4	222	1.4596
5a	CH_3	$COCH_3$	99.1	−76.7	200	1.4550
5b	C_2H_5		97.2	−73.0	200	1.4534
5c	1-C_4H_9		100	−84.2	212	1.4541
5d	2-$(C_2H_5)C_6H_{12}$		98.7	−80.3	234	1.4561

[a] $x = 7,\ y = 8;\ x = 8,\ y = 7.$

[b] The elemental analyses were within normal limits for all 14 compounds, with an average discrepancy between found and calculated values of 0.21 for percent carbon and 0.23 for percent hydrogen.

[c] At 0.005 mm.

[d] C_3H_6 =


acetone, 50 ml dimethoxypropane (DMP), and 0.1 g *p*-toluenesulfonic acid was stirred at room temperature for 0.5 hr, then let stand overnight. After addition of 2 ml 10% sodium hydroxide solution, the mixture was stripped on the rotary evaporator. The residue was dissolved in 500 ml of petroleum ether (boiling range 38.0-45.9 C), washed with 2 x 100 ml water, filtered, and dried over magnesium sulfate. Filtration and evaporation gave 113 g product, 78% **3** (GLC).

Methyl 9,9(10,10)-Bis(hydroxymethyl)octadecanoate Acetone Acetal (4a)

Solution of 213 g **3** (98.7%; 210.2 g, 0.55 mole), 300 ml methanol, 750 ml DMP, and 0.4 g *p*-toluenesulfonic acid was stirred at room temperature overnight. Another 0.2 g *p*-toluenesulfonic acid was added, the solution relfuxed for 1 hr and again stirred overnight. Solid sodium bicarbonate was added and the mixture stirred vigorously for 15 min, filtered, and stripped on the rotary evaporator. The residue was dissolved in 1000 ml petroleum ether, washed with 4 x 250 ml water, filtered, and dried over magnesium sulfate. Filtration and evaporation left 216 g of product, 94.5% **4a** by GLC. This was distilled at 187-220 C/0.01-0.02 mm to give 158 g of distillate, 94.8% **4a**. There was 50 g (23.7%) pot residue.

In another experiment, a solution of 215 g of undistilled product containing 90.9% **4a** in 1000 ml petroleum ether was washed with 2 x 250 ml water, 2 x 250 ml 5% sodium hydroxide solution, 7 x 250 ml water, 250 ml 5% sulfuric acid, and 3 x 250 ml water, filtered, and dried over magnesium sulfate. Filtration and evaporation left 167 g of product containing 96.4% **4a**. The basic washes were acidified and extracted with ether to give 46 g of material containing 5.9% **1**, 64.2% **3**, and 13.3% **4a**. Distillation of the main product at 196-206 C/0.005 mm gave 136 g distillate, 99.9% **4a**. There was 26 g (16%) pot residue. A sample of **4a** was redistilled for analysis.

Ethyl 9,9(10,10)-Bis(hydroxymethyl)octadecanoate Acetone Acetal (4b)

Saponification of 100 g of distilled **4a** gave 88.3 g **3** (96.3%, 86.1 g, 0.22 mole) which was dissolved in 500 ml absolute ethanol. *p*-Toluenesulfonic acid (1 g) was added and the solution refluxed for 2 hr. Solid sodium bicarbonate was added and the solution stripped on the rotary evaporator. The residue was dissolved in 500 ml diethyl ether and the ether solution washed with 3 x 100 ml water, 100 ml 10% sulfuric acid, and 4 x 100 ml water, filtered, and dried over magnesium sulfate. Filtration and evaporation left 84.4 g product containing 69.9% **2b** and 27.0% **4b** (GLC). This was dissolved in 500 ml acetone containing 50 ml DMP and 0.2 g *p*-toluenesulfonic acid. The solution was stirred at room temperature for 2 hr. Solid sodium bicarbonate was added and acetone and DMP were removed by the rotary evaporator. The residue was dissolved in 500 ml petroleum ether and the solution washed with 2 x 100 ml water, 2 x 100 ml 5% sodium hydroxide solution, 4 x 100 ml water, 100 ml 5% sulfuric acid, and 3 x 100 ml water. It was then filtered and dried over magnesium sulfate. Filtration and evaporation left 70.8 g product, 97.5% **4b** (GLC). This was distilled at 171-186 C/0.005 mm to give 67.5 g **4b**, 99.3% (GLC). The combined basic washes were acidified with 10% sulfuric acid and extracted with ether to give 12.7 g material containing 67.5% **4b** and 20.3% **3**.

1-Butyl 9,9(10,10)-Bis(acetoxymethyl)octadecanoate (5c)

A solution of 14 g **2c** (97.8%, prepared by hydrolysis of **4c**) in 100 ml acetic anhydride was stirred magnetically at room temperature. One drop of concentrated sulfuric acid was added. The temperature rose to 43 C in 2 min. Stirring was continued for 2.5 hr. Reaction mixture was stripped on the rotary evaporator and the residue dissolved in 200 ml petroleum ether. This solution was washed with 2 x 50 ml water, 50 ml 10% sodium hydroxide solution, and 3 x 50 ml water, filtered, and dried over magnesium sulfate. Filtration and evaporation left 14.7 g liquid, 95.2% **5c**. This was combined with product from another reaction, run under the same conditions, and the composite distilled at 226-240 C/0.005 mm to give 24.9 g distillate containing 96.9% **5c**. There was 0.6 g (2.4%) pot residue. A sample was redistilled for analysis.

The above reaction was repeated using 30 g **4c** (97.2%), 150 ml acetic anhydride, and 0.7 ml concentrated sulfuric

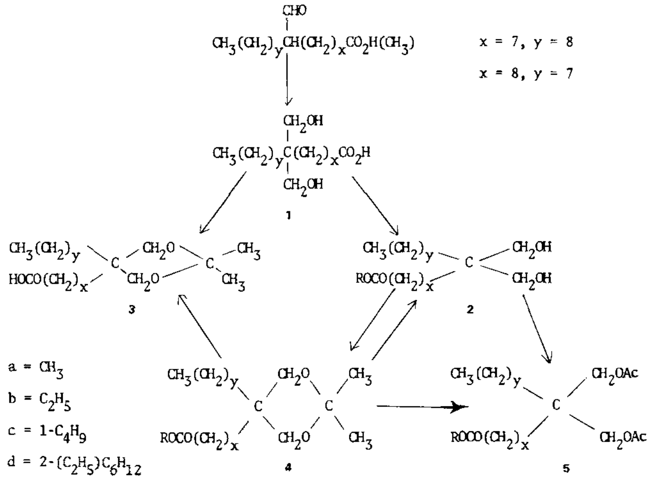


FIG. 1. Synthetic Routes.

acid. The temperature rose to 32 C in 12 min. The product contained 87.4% **5c** and 6.2% **2c**. It distilled at 196-234 C/0.002-0.003 mm to give a dark red distillate containing 89.2% **5c**. There was 12.4% pot residue. Redistillation gave a yellow product.

Samples for Characterization

A pure sample of **1** was prepared by refluxing a mixture of 10 g methyl 9,9(10,10)-bis(acetoxymethyl)octadecanoate, 100 ml methanol, and 5 g sodium hydroxide for 4 hr. The mixture was diluted with 100 ml water, acidified with 15% sulfuric acid, and stripped of methanol on the rotary evaporator. The residue was dissolved in 100 ml ether and the ether solution washed with 6 x 50 ml water, filtered, and dried over magnesium sulfate. Filtration and evaporation of the ether gave 7.8 g **1**, 99.9% (GLC).

A mixture of 10 g of acetone acetal of **2a**, 150 ml water, and 5 drops concentrated sulfuric acid was heated to boiling for 15 min. The mixture was cooled and extracted with 2 x 100 ml ether. The combined extracts were washed with 2 x 50 ml water, filtered, and dried over magnesium sulfate. Filtration and evaporation left 8.2 g **2a**, 100% (GLC).

Ten grams of **4a** was saponified in the same way as **5a**. The product was 8.6 g **3**, 100% (GLC).

Spectroscopic Analyses

Methyl 9,9(10,10)-bis(hydroxymethyloctadecanoate) (**2a**), its acetone acetal (**4a**), and its acetyl derivative (**5a**) were analyzed by infrared (IR), nuclear magnetic resonance (NMR) and mass spectroscopy (MS). These methyl esters were chosen to minimize complications due to longer chain alkyl groups. Spectra obtained were consistent with the assigned structures.

2a. IR: broad band at 3380 cm^{-1} (CH_2OH); NMR: δ 3.51 bs ($HOC\underline{H}_2CC\underline{H}_2OH$), δ 2.66 bs [$O\underline{H}(2H)$]; MS: (70 ev) m/e (fragment, relative intensity in percent): 359 (M + 1, 1.83), 310 [$CH_3(CH_2)_8\overset{CH_2}{\overset{\|}{C}}(CH_2)_7CO_2CH_3$, 59.96], 197 [$CH_2{=}C(CH_2)_8CO_2CH_3$, 11.89], 183 [$CH_2{=}C(CH_2)_7CO_2CH_3$, 11.04], 157 [$(CH_2)_7CO_2CH_3$, 22.03].

4a. IR: bands at 1195 cm^{-1} [$C(CH_3)_2$] and 1095 cm^{-1} (C-O-C); NMR: δ 3.51 bs ($OC\underline{H}_2CC\underline{H}_2O$), δ 1.38 s ($C\underline{H}_3$-C-$C\underline{H}_3$); MS: 383 (M - 15, CH_3, 85.86), 157 [$(CH_2)_7CO_2CH_3$, 20.25].

5a. IR: strong absorbance at 1740 cm^{-1} and 1230 cm^{-1} (CH_3COO); NMR: δ 3.88 bs ($CH_3COOC\underline{H}_2CC\underline{H}_2OCOCH_3$), δ 2.02 s [$C\underline{H}_3CO(6H)$]; MS: 411 (M - 31, CH_3O, 4.92), 369 (M - 73, $CH_3CO_2CH_2$, 25.61), 322 [$CH_3(CH_2)_8\overset{CH-CH}{\overset{\diagdown\,\diagup}{C}}(CH_2)_7CO_2CH_3$, 19.34], 309 [$CH_3(CH_2)_8\overset{CH}{\overset{\|}{C}}(CH_2)_7CO_2CH_3$, 16.23], 157 [$(CH_2)_7CO_2CH_3$, 3.05].

All. IR: usual long-chain ester bands; NMR: δ 3.62-3.64 s ($CO_2C\underline{H}_3$), δ 2.28-2.29 t ($C\underline{H}_2CO_2$), δ 1.25-1.26 m [$-(CH_2)_{7(8)}-$], δ 0.86-0.87 m ($C\underline{H}_3$).

RESULTS AND DISCUSSION

9,9(10,10)-Bis(hydroxymethyl)octadecanoic acid (1)

Figure 1 diagrams the primary routes used to synthesize the compounds reported in this paper.

FSA reacted with formaldehyde in basic solution through a Tollens condensation followed by a crossed Cannizzaro reaction to give **1**. The procedure used was that of Moore and Pryde (4), slightly modified. Because it was impractical to add solid FSA to the formaldehyde solution, FSA was dissolved in methanol. The formaldehyde solution contained enough sodium hydroxide to neutralize the FSA as well as the formic acid formed by the Cannizzaro reaction. As an alternative, FSA was dissolved in a sodium hydroxide solution which contained only slightly more than the equivalent amount of base required to dissolve the acid. Conversion to **1** was essentially complete in about 2 hr at room temperature in methanol and about 4 hr in water. Practically, the reaction mixture was usually allowed to stand overnight with no apparent effect on the product.

The reaction was notable for absence of side reactions. A sample of FSA in alkaline solution was essentially unchanged after 71 hr. However, the product itself had a tendency to undergo self-esterification during derivatization and during storage as explained subsequently.

Attempts to follow the course of the reaction by GLC analysis were not successful. Silylation (6,7) required for analysis of **1** caused extensive decomposition of FSA, making it impossible to determine how much remained unreacted. Conversely, simple esterification with diazomethane, which would have been satisfactory for FSA, gave a product that was not sufficiently volatile for GLC.

Some preliminary experiments with MFS indicated that very little reaction took place, and that only with saponified ester, probably because of the insolubility of the ester. We later found, under conditions used with FSA, that a methanolic solution of MFS was completely saponified and converted to **1**. As with FSA, analysis during reaction was complicated by decomposition of MFS by silylating agent. Some **2a** may have been formed during early stages of the reaction, but quantitative determination was not possible.

FSA and MFS used in these experiments ranged in purity from 70 to 98%. Principal impurities were stearic and carboxystearic acids. These compounds were carried through in preparation of **1** and were still present in the product, together with whatever byproducts were formed. An advantage of using methanol as reaction medium was the partial insolubility of sodium stearate, which could be removed by filtration.

Reaction products containing **1** were very viscous liquids which did not crystallize. Most of the reactions to be described were performed with these products. A pure sample of **1** was obtained by saponification of **5a**. Its properties were essentially those of the reaction products.

On extended storage, **1** underwent intermolecular esterification to nonvolatile products, thus apparently altering its composition by GLC. In one stored sample, GLC indicated the major components to be 52% **1** and 28% carboxystearic acid (CSA), with much sample retained on the GLC column. After saponification the composition was 84% **1**, 7% CSA. Finally the saponified sample was warmed on the steam bath for 8 hr and then found to contain 64% **1**, 25%

CSA. Accordingly, **1** was prepared shortly before use and stored in the freezer.

Esterification

Esterification of products containing **1** by standard procedures presented no obvious problems. An unexpected problem did arise in analysis of some esters, particularly **2a**.

GLC analyses of **2a**, silylated by the standard procedure (7), frequently showed two peaks, differing in retention time by about 2 min, representing disilylated and monosilylated derivatives. Longer silylation time altered peak ratios, but as long as 90 min heating was required to eliminate the second peak. Addition of a small quantity of water (5-10 μl/30 mg sample) promoted complete silylation in the usual 10 min. This partial silylation was not observed with **1**.

Acetalation

Acetalation of **1** or its esters was easily accomplished with acetone and *p*-toluenesulfonic acid catalyst at room temperature. Addition of a small amount of 2,2-dimethoxypropane (DMP) to scavenge water of reaction ensured complete acetalation. Simultaneous esterification and acetalation could be accomplished with a methanol-DMP mixture to give **4a**.

Ester-acetal **4a** could be distilled under vacuum. However, distillation was preceded by evolution of uncondensable fumes and left 20-25% undistillable residue. Redistillation went smoothly without fuming and left only nominal residue, indicating that these problems were not caused by the ester-acetal itself but probably by oligomers formed during esterification.

Results were essentially the same whether ester-acetal **4a** was prepared directly from **1**, from methyl ester **2a**, or from acid-acetal **3**, as well as in the preparation of the other ester-acetals. Extraction of crude ester-acetal with base before distillation decreased fuming and residue formation, but overall yield remained about the same. Extraction removed **1**, unacetalated ester **2**, acid-acetal **3**, and other acidic material, but was accompanied by formation of extremely stable emulsions which included some product. The extracted material could be recovered and should be recyclable. Thorough washing of the extracted product was needed to remove all residual alkali.

Saponification of pot residue primarily gave **1**. Obviously during esterification, there was some self-esterification of **1** with itself. We hoped to avoid this self-esterification by first preparing **3**, but saponification showed that as much as 9% of **1** must have self-esterified during acetalation. Esterification of **3** with higher alcohols led to extensive acetal alcoholsis—the extent varying with the alcohol and esterification procedure used—thus again permitting some self-esterification of **1**. Probably even during esterification of **3** with methanol-DMP there was an equilibrium among **2a**, **3**, and **4a** that permitted self-esterification. However, when **3** was obtained by saponification of distilled **4a** and reesterified with methanol-DMP, the product left only 3% residue on distillation. Distillation of **4b** prepared from **3** so obtained left only 2.9% residue.

Ester-acetals such as **4** offer the opportunity for selective reactions at either functional group, as we have shown earlier for the acetals of alkyl azelaaldehydates (8). As already mentioned, saponification of **4a** gave **3**. Acid hydrolysis of **4** gave corresponding esters **2**. However, we did not investigate transesterification of **4** catalyzed by alkoxides, an alternate route to higher esters.

Acetylation

Sulfuric acid-catalyzed acetylation (9) was utilized to prepare bis(acetoxymethyl) esters, **5**. When methyl ester **2a**, prepared by esterification of **1** was acetylated, distillation of the product was accompanied by fuming and residue formation as described for methyl ester-acetal **4a**. However, when ester **2**, obtained by hydrolysis of ester-acetal **4**, was acetylated by the same procedure, distillation proceeded smoothly with minimal residue formation.

It was possible to acetylate ester acetals **4** directly. To do this, more sulfuric acid catalyst and longer reaction times were required. The reaction was only slightly exothermic, as compared with the reaction with **2**, and products were yellow, probably because of condensation products of the liberated acetone.

The successful preparation of acetal and acetyl esters, **4** and **5**, from acid-acetal **3** or ester **2** obtained by saponification or hydrolysis of methyl ester-acetal **4a** led to a standard laboratory procedure: **4a** is prepared and distilled for use as starting material for preparation of other esters, their acetal and acetyl derivatives, as illustrated by preparation of ethyl ester-acetal **4b** and 1-butyl bis(acetoxymethyl)octadecanoate **5c** in Experimental Procedures.

Acetal and acetyl esters **4** and **5** remain liquid at atmospheric pressure over an extremely wide temperature range, from <-70 to ca. 400 C, the boiling point estimated from the 200 C boiling point at 0.005 mm. As derivatives of a 2,2-disubstituted-1,3-propanediol, they would be expected to be particularly stable to heat and oxidation. On repeated distillations, they have shown no indication of decomposition.

We anticipate that these materials, derived from renewable agricultural resources by simple, widely used reactions with inexpensive reagents, will find many applications where stable organic liquids, primarily derived from irreplaceable petroleum, are now used. Some specific applications will be reported elsewhere. Appropriate choice of acetal and ester groups should permit tailoring products with specific properties for particular uses.

ACKNOWLEDGMENTS

E.N. Frankel supplied FSA and MFS; W.E. Neff obtained TMA data; F.L. Thomas helped with analyses; C.E. Johnson, B.R. Heaton, W.P. Schroeder, and L.C. Copes provided microanalysis; D. Weisleder did NMR analyses; W.K. Rohwedder obtained mass spectra.

REFERENCES

1. Nielsen, A.T., and W.J. Houlihan, Org. React. 16:15 (1968).
2. Geissman, T.A., Ibid 2:99 (1944).
3. Walker, J.F., in "The Encyclopedia of Chemistry," Third edition, edited by C.A. Hampel and G.G. Hawley, VanNostrand Reinhold Co., New York, NY, 1973, p. 43.
4. Moore, D.J., and E.H. Pryde, JAOCS 45:517 (1968).
5. Frankel, E.N., Ibid. 48:248 (1971).
6. Pierce, A.E., "Silylation of Organic Compounds," Pierce Chemical Co., Rockford, IL, 1968.
7. Miller, W.R., W.E. Neff, E.N. Frankel, and E.H. Pryde, JAOCS 51:427 (1974).
8. Pryde, E.H., D.J. Moore, H.M. Teeter, and J.C. Cowan, J. Chem. Eng. Data 10:62 (1965).
9. Burgstahler, A.W., and Z.J. Bithus, Org. Syn. Coll., 5:592 (1973).

[Received November 3, 1976]