Chemical Intermediates and Derivatives from Oleyl Alcohol

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Abstract

Several series of compounds were prepared from oleyl alcohol which may prove useful as lubricants and plasticizers. The reactions involved addition to the double bond and replacement of the hydroxyl moiety. One series of compounds is characterized 1-R′, 9(10)R octadecane where 1-R′ signifies the replacement of hydroxyl by ethoxy, *tert*-butylphenyl, *tert*-butoxy and phenyl. Examples of additions across the double bond 9(10)R, include hydrogen, methoxy, *tert*-butoxy, *tert*-butylphenyl, and phenyl. Other test series were 9(10)-R, 27(28)-R-hexatriacontane and *bis* [9(10)-R-octadecyl] ether where R signifies additions across a pair of double bonds. Additions in these series include methoxy, ethoxy, *tert*-butoxy, *tert*-butylphenyl, 2-ethylhexoxy, and phenyl.

Derivatives of octadecane were fluid and several had fairly low pour points. The derivatives of hexatriacontane and dioctadecyl ether were either low-melting solids or liquids. Details concerning the synthesis and several physical properties are presented.

Introduction

TALLOW IS AN ATTRACTIVELY priced raw material. Supplies have been abundant in recent years, and there is no reason to believe that this situation will be changed in the near future.

The objectives of much governmental and industrial research have been directed toward increasing the utilization of tallow. We have prepared derivatives that appear to have commercial potential.

Oleyl alcohol, a major by-product of tallow was used in this study. Oleyl alcohol has two points of reactivity which are the hydroxyl group and the carbon to carbon double bond at the 9-position. Reactions involving the addition across a carbon to carbon double bond are well known. Iodine and thiocyanogen numbers are simple examples of such reactions which are useful in analytical procedures. The additions to the double bond reported here were concerned principally with aryl and alkoxy substitutions. Reactions involving the hydroxyl group are equally numerous and well known. We have been principally concerned with those reactions involving reduction to the hydrocarbon and dimerization. A number of derivatives have been prepared, many of which have not been previously reported. These compounds are substituted octadecanes, hexatriacontanes and dioctadecyl ethers.

Additions to the unsaturated groups can be expected to result in isomer formation and some shifting of the double bond. No attempts were made to separate mixtures of isomers or confirm their nature by structural analysis.

Experimental

Starting Materials and Intermediates

The oleyl alcohol used was the "Novol" grade, Croda, Inc., I.V. 91.1, N_D^{30} 1.4571. Oleyl alcohol was converted to 9(10)-phenyloctadecanol by Friedel-Crafts reaction with benzene and aluminum chloride (1). The compound had a bp 198–204C/1 mm; N_D^{20} 1.4910. The phenyloctadecanol then was converted to the bromide by reaction with hydrogen bromide as follows: Anhydrous hydrogen bromide was added slowly over a period of four hr to 9(10)-phenyloctadecanol at 100–110C. The mixture was then washed successively with cold H_2SO_4, 50% methyl alcohol, 15% ammonia, and finally with 50% methyl alcohol. The product was distilled and collected as a clear yellow oil at 185–190C/0.2 mm; N_D^{20} 1.4950. *Anal.* Calcd. for $C_{24}H_{41}Br$: Br, 19.5. Found: 19.3. *Tert*-butybenzene (Eastman Kodak) had a bp 167.5–170.5C and was used without further purification. The 9(10)-*tert*-butylphenyloctadecanol was obtained as an *amber fluorescent oil. It had a bp* 211–215C/0.8 mm; N_D^{20} 1.4975. The preparation of 9(10)-*tert*-butylphenyloctadecyl bromide was identical with that described above for the unsubstituted phenyl derivative. The bromide was collected as the fraction distilling at 215–220C/0.2 mm. *Anal.* Calcd. for $C_{28}H_{49}Br$: Br, 17.2. Found: 17.3.

Oleyl bromide was prepared by reacting oleyl alcohol with phosphorous tribromide in carbon tetrachloride at −10 to 0C (2). After removal of the CCl_4, the residue was distilled through a 30 cm Vigreaux column and the fraction boiling at 175–180C/0.5 mm was collected. The distillate had a trace odor of phosphine. *Anal.* Calcd. for $C_{18}H_{35}Br$: Br, 24.1. Found: 23.5.

Several attempts were made to synthesize dioleyl ether from oleyl alcohol using *p*-toluenesulfonic acid as catalyst (3). The method resulted in low yields. The ether was readily prepared however, with a BF_3 catalyst (4). Into a 2-1 round bottom flask, fitted with a reflux condenser, mechanical stirrer, and $CaCl_2$ drying tube, were placed oleyl alcohol (537 g, 2.0 mole) and boron trifluoride ethyl ether (72 g, 0.51 mole). The solution was refluxed at 180C for 4 hr, then cooled to room temperature. The crude product was extracted with ethyl ether and washed with water until neutral. The ether extract was dried over anhydrous Na_2SO_4. After removing the solvent, the product was collected as a viscous oil, bp 278–290C/1 mm. The distillate was recrystallized from acetone to yield a white solid, mp 34.5–35C, N_D^{38} 1.4550. The hydroxyl value was 3.9. The yield was 122.5 g.

The dioleyl ether was converted to *bis*[9(10)-bromoöctadecyl] ether by hydrobromination with a benzoyl peroxide catalyst. Free radical hydrobromination studies of fatty derivatives have previously been reported (5). The addition of HBr was carried out for 6 hr at room temperature. The product was washed with water until neutral and then dried over $CaCl_2$. *Anal.* Calcd. for $C_{36}H_{72}OBr_2$: Br, 23.5. Found: 22.0.

Loev and Dawson (6) obtained what they believed to be 9,27-hexatriacontadiene as a by-product of the hydrolysis of oleyl magnesium bromide. Efforts to couple oleyl *p*-toluenesulfonate with magnesium and iodine in anhydrous ether were unsuccessful. However, fair yields were obtained by reacting oleyl bromide and sodium in an inert solvent.

A mixture of sodium (17.5 g, 0.76 mole) and 200 ml of dry toluene was heated under reflux until a fine suspension of sodium was obtained. Over a period of 1 hr, oleyl bromide (165 g, 0.5 mole) was added in small increments. The mixture was refluxed for 24 hr. Excess sodium was decomposed with cold dilute HCl, and the toluene layer was washed with saturated solutions of NaCl, $NaHCO_3$, and water. The toluene layer was dried over anhydrous Na_2SO_4 and the solvent was removed by distillation. The crude residue, 111.5 g, was recrystallized from acetone at −25C to yield 26.1 g of a wax-like diene mp 44–45C and 58.0 g of an acetone insoluble oil. Fractionation of the latter did not increase the yield.

Hydrobromination of 9,27-hexatriacontadiene was carried out in benzene at room temperature with a benzoyl peroxide catalyst. The product was a dark amber oil. *Anal.* Calcd. for $C_{36}H_{72}Br_2$:Br, 24.1. Found: 22.9.

Preparation of Derivatives

Substituted Octadecanes

9(10)-Aryl Derivatives. Preparation of aryl substituted octadecanes is typified by the synthesis of 9(10)-phenyloctadecane (1).

Phenyloctadecyl bromide (110 g, 0.27 mole), was added dropwise during 30 min to magnesium turnings (7.3 g, 0.3 mole) in 500 ml of anhydrous ether. The mixture was warmed slightly to initiate reaction. After all the bromide had been added, the reaction was refluxed for 4 hr. The flask was surrounded by an ice-bath, and the contents were hydrolyzed by the careful addition of 100 ml of a cooled 14% NH_4Cl solution, followed by 100 ml of 5% HCl. The ether solution was washed until neutral, and then dried over anhydrous Na_2SO_4. The product, 9(10)-phenyloctadecane was obtained as a colorless liquid *Anal.* Calcd. for $C_{24}H_{42}$:C, 87.2; H, 12.8. Found C, 85.9, H, 13.2. Another derivative, 9(10)-*tert*-butylphenyloctadecane was similarly prepared. The compound was a light yellow oil. *Anal.* Calcd. for $C_{28}H_{50}$:C, 87.0, H, 13.0. Found C, 86.2; H, 13.1.

1, 9(10)-Diaryl Derivatives. Preparation of 1, 9(10)-diphenyloctadecane was accomplished by Friedel-Crafts alkylations at both the terminal halide and double bond positions. Oleyl bromide, (191.9 g, 0.58 mole) was dssolved in 250 ml of anhydrous benzene and added slowly over a period of 4 hr to a stirred solution of anhydrous aluminum chloride (170 g, 1.28 mole) in 750 ml of benzene. The reaction was maintained at a temperature of 35C during the addition. The mixture was stirred for 10 hr at 65–70C, then cooled and hydrolyzed with cold dilute HCl. The benzene was removed by steam distillation and the product obtained as a red oil. *Anal.* Calcd. for $C_{30}H_{46}$: C, 88.6; H, 11.4. Found C, 88.9; H, 11.0. Similarly, 1, 9(10)-di-*tert*-butylphenylocadecane was prepared from *tert*-butylbenzene and oleyl bromide. The product was obtained as a highly fluorescent red oil boiling at 185–202C/0.2 mm; N^{20}_D 1.5880. *Anal.* Calcd. for $C_{38}H_{62}$: C, 88.0; H, 12.0. Found C, 86.9; H, 12.2.

Ether Derivatives. 9(10)-ethoxyoctadecane was prepared by the reaction of sodium ethoxide and hydrobrominated 9-octadecene. The 9-octadecene bp 125–137C/1.0 mm was obtained by the hydrolysis of a Grignard compound prepared from oleyl bromide. The residual products were purified by passing a hexane solution through three chromatographic columns of alumina. After removing the solvent, the 9(10)-ethoxyoctadecane was obtained as a clear yellow oil; N^{31}_D 1.4477. *Anal.* Calcd. for $C_{20}H_{42}O$: C, 80.2; H, 14.2. Found C, 79.7; H, 13.9.

The 1, 9(10)-di-*tert*-butoxy derivative of octadecane was also prepared from oleyl bromide. The procedure involved a Williamson etherification at the terminal position, hydrobromination at the 9, 10 position and an additional Williamson reaction with the *tert*-butyl alcoholate. *Anal.* Calcd. for $C_{26}H_{54}O_2$: C, 78.3; H, 13.7. Found C, 78.0; H, 13.5.

Reaction of 9(10)-phenyloctadecyl bromide and sodium *tert*-butoxide yielded 65% of 1-*tert*-butoxy 9(10)-phenyloctadecane. *Anal.* Calcd. for $C_{28}H_{50}O$: C, 83.5; H, 12.5. Found C, 82.9; H, 12.9.

Preparation of 1-methoxy 9(10)-*tert*-butoxyoctadecane was accomplished by first reacting oleyl bromide with sodium methoxide to obtain 1-methoxy 9-octadecene; bp 136–140C/0.5 mm; N^{20}_D 1.4510. The product was hydrobrominated and 1-methoxy 9(10)-bromooctadecane was obtained; bp 178–190C/0.2 mm, N^{20}_D 1.4715. The reaction of the latter with sodium *tert*-butoxide resulted in a 30% yield of 1-methoxy-9(10)-*tert*-butoxyoctadecane. *Anal.* Calcd. for $C_{23}H_{48}O_2$: C, 77.9; H, 13.6. Found C, 77.2; H, 12.9.

Substituted Hexatriacontanes

Aryl Derivatives. Diphenylhexatriacontane was prepared by a modified Wurtz reaction using metallic sodium and aryl substituted octadecyl bromide. Into a stirred suspension of dry toluene and fresh sodium (1.15 g, 0.05 mole) at reflux temperature was added 9(10)-phenyloctadecyl bromide (81.8 g, 0.2 mole). The reaction was refluxed for 24 hr. The reaction proceeded with the development of the characteristic blue color. Cold dilute HCl was then added to decompose the excess sodium and then the solution was washed with water until neutral and dried over $CaCl_2$. The toluene was removed by vacuum distillation. The product was purified by dissolving in hexane and was passed through three chromatographic columns of alumina. The product was a clear yellow oil with a nil iodine value. The di-*tert*-butylphenyl derivative was similarly obtained.

Ether Derivatives. The following procedure was used for the preparation 9(10), 27(28)-dimethoxyhexatriacontane.

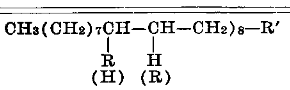
Into a 300 ml round-bottom flask, equipped with a mechanical stirrer and a reflux condenser, fitted with a $CaCl_2$ drying tube, were placed 9(10), 27(28)-dibromohexatriacontane (40.0 g, 0.06 more) and 6.5 g of sodium methoxide in 15 ml of anhydrous CH_3OH. When the initial reaction had subsided, the reaction was refluxed on a water bath for 4 hr. The reaction was cooled and 20 ml of ice water added. The crude product was extracted with ether, then washed with water until a test for bromide was negative. The ether layer was dried over $CaCl_2$ and the ether removed to yield 9(10), 27(28)-dimethoxyhexatriacontane. *Anal.* Calcd. for $C_{38}H_{78}O_2$: C, 80.5; H, 13.9. Found C, 79.6; H, 13.5. The di-2-ethylhexyl ether derivative was similarly prepared and recrystallized first from ethanol and then from acetone and had a mp 18C. *Anal.* Calcd. for $C_{52}H_{106}O_2$: C, 81.8; H, 14.0. Found C, 82.6; H, 13.3.

Substituted Dioctadecyl Ether Compounds

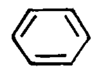
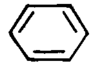
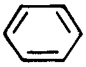
Ether Derivatives. Four diether derivatives of dioctadecyl ether were prepared by reacting the sodium

TABLE I

Pour Point, Boiling Point, Index of Refraction, and Viscosity of Substituted Octadecanes



$CH_3(CH_2)_7\underset{\substack{R\\(H)}}{CH}-\underset{\substack{H\\(R)}}{CH}-(CH_2)_8-R'$

R	R′	Pour point, C	Boiling point, C	Index of refraction	Viscosity, cs. 100F
OC_2H_5	H	−24	....	N_D^{31} 1.4477	4.4
 — $C(CH_3)_3$	H	−10	165–180/0.5 mm	N_D^{20} 1.4900	15.4
$OC(CH_3)_3$	$OC(CH_3)_3$	−31	170–182/0.2 mm	....	8.9
	$OC(CH_3)_3$	−26	153–168/0.2 mm	N_D^{20} 1.4590	13.6
	H	−9	166–172/0.5 mm	N_D^{20} 1.4850	11.0
$OC(CH_3)_3$	OCH_3	+7	178–190/0.2 mm	N_D^{20} 1.4650	5.9
 — $C(CH_3)_3$	 — $C(CH_3)_3$	−37	185–202/0.2 mm	N_D^{20} 1.5880	25.4
		−31	178–189/0.2 mm	N_D^{20} 1.5472	19.7

alcoholate and bis [9(10)-bromoöctadecyl] ether. The dimethoxy derivative was prepared thus:

Into a three-neck flask, equipped with a mechanical stirrer and reflux condenser fitted with a drying tube, were added with stirring *bis* [9(10)-bromoöctadecyl] ether (102.0 g, 0.15 mole) and sodium methoxide (16.2 g, 0.3 mole). After the initial reaction had subsided, 20 ml of dry CH_3OH was added and the mixture refluxed on a water bath for 9 hr. The reaction mixture was cooled, and cold water cautiously added. The product was taken up in ether and washed with water, saturated $NaHCO_3$ solution, and again with water. The solution was dried over anhydrous Na_2SO_4 and the ether evaporated to give an amber oil. The product was treated with decolorizing charcoal and purified by absorption from hexane solution on an alumina column. The final product was a light amber oil, N_D^{30} 1.4634. *Anal.* Calcd. for $C_{38}H_{78}O_3$: C, 78.3; H, 13.5. Found C, 78.2; H, 13.1.

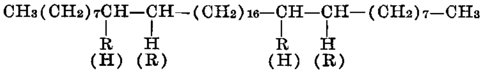
Similarly, the other homologs were prepared by reacting the sodoxo derivatives (prepared in situ) and the *bis* [9(10)-bromoöctadecy] ether. The diethoxy, and the di-2-ethylhexyl ether derivatives were also prepared.

Aryl Derivative. The following procedure was used to prepare *bis* [9(10)-*tert*-butylphenyloctadecyl] ether:

Di-*n*-oleyl ether (145 g, 0.25 mole) dissolved in 250 ml of *tert*-butylbenzene was added to a stirred solution of anhydrous $AlCl_3$ (82.6 g, 0.62 mole) in 250 ml of *tert*-butylbenzene. The temperature was not allowed to exceed 35C during the addition. The mixture was then heated and stirred for 10 hr at 80C, cooled, and hydrolyzed with dilute HCl. The excess *tert*-butylbenzene was removed by steam distillation and the product taken up in ether, and dried over anhydrous Na_2SO_4. The product was obtained as a red oil distilling at 215–235C/0.5 mm. *Anal.* Calcd. for $C_{56}H_{98}O$: C, 85.5; H, 12.5. Found C, 85.1; H, 11.4.

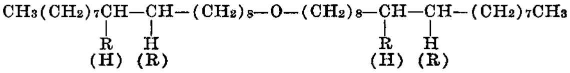
TABLE II

Pour Point, Index of Refraction and Viscosity of Some Substituted Hexatriacontanes and Dioctadecyl Ethers

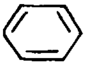


$CH_3(CH_2)_7\underset{\substack{R\\(H)}}{CH}-\underset{\substack{H\\(R)}}{CH}-(CH_2)_{16}-\underset{\substack{R\\(H)}}{CH}-\underset{\substack{H\\(R)}}{CH}-(CH_2)_7-CH_3$

R	Pour point, C	Index of refraction	Viscosity, cs. 100F
OCH_3	>0	N_D^{30} 1.4654	11.6
 — $C(CH_3)_3$	−18	N_D^{20} 1.4910	22.4
OC_8H_{17}[a]	+7	....	16.7
	<0	N_D^{30} 1.4871	17.7



$CH_3(CH_2)_7\underset{\substack{R\\(H)}}{CH}-\underset{\substack{H\\(R)}}{CH}-(CH_2)_8-O-(CH_2)_8-\underset{\substack{R\\(H)}}{CH}-\underset{\substack{H\\(R)}}{CH}-(CH_2)_7CH_3$

R	Pour point, C	Index of refraction	Viscosity, cs. 100F
OCH_3	>0	N_D^{30} 1.4634	17.0
OC_8H_{17}[a]	+18	N_D^{30} 1.4635	22.7
$OC(CH_3)_3$	+10	N_D^{30} 1.4645	19.6
OC_2H_5	+7	N_D^{30} 1.4641	17.3
 — $C(CH_3)_3$	−4	....	40.0

[a] 2-Ethylhexyl ether.

Discussion

The series of compounds described demonstrate the almost endless possibilities for the synthesis of new materials from a readily available raw material.

Many of the derivatives synthesized from oleyl alcohol reported here should find sufficient interest in various areas of research. Application to the lubricant field immediately comes to mind. Requirements for such products generally include low pour point, low volatility, good thermal stability, high viscosity index, stability to oxidation, absence of objectionable decomposition residues, resistance to hydrolysis, miscibility with petroleum lubricants and additives, and low material cost. Several physical properties of the compounds synthesized are given in Tables I and II. The boiling points appeared sufficiently high to meet volatility requirements. The absence of double bond and additions of the stabilizing *tert*-butylphenyl groups should impart oxidation resistant characteristics to the structure.

Other possible uses for the compounds include plasticizers, special solvents, viscosity modifiers, and flame retardancy as exemplified by the bromide derivatives.

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