Nonvolatile *alpha*-Branched Chain Fatty Esters. II.[1]

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Abstract

A group of nonvolatile *alpha*-branched esters was prepared by the di-tertiary butyl peroxide-promoted addition of normal esters to terminal olefins containing methyl branches or aryl groups. Methyl stearate was added to 3,7-dimethyl-1-octene, 3,5,5-trimethyl-1-hexene, and 4-phenyl-1-butene. The reaction with 2,4,4-trimethyl-1-pentene, a terminal alkene with a methyl branch at the internal ethylenic carbon, was not successful. Benzyl 2-(4-phenylbutyl)octadecanoate was prepared by transesterification of the corresponding methyl ester. Benzyl 2,2-dimethylpropanoate, which has no α-hydrogen in the acyl portion of the molecule, was added to 1-hexadecene to form α-hexadecylbenzyl 2,2-dimethylpropanoate. Lubricant evaluation data were obtained on the above compounds.

Introduction

RECENT COMMUNICATIONS (1–3) from this laboratory have described the preparation, properties, and bench evaluation as lubricants of some *alpha*-branched chain esters. For the most part, these esters were prepared by the free radical induced addition of long-chain saturated fatty esters to straight-chain terminal olefins. The present paper is an extension of this investigation and describes the synthesis and properties of some similarly branched esters, using branched-chain terminal olefins. Included among the new compounds is an example of a diester having both of the acyl groups *alpha*-branched and no *beta* hydrogens in the alcohol portion of the ester.

The hydrolytic stability of the *alpha*-branched esters gives them considerable practical potential. Although the derivatives reported previously were aliphatic in nature, the present series includes examples that contain aryl groups in the side chain and/or the alcohol portion.

The synthetic procedure for making the compounds, originally described by Nikishin et al. (4), involves the abstraction of an α-hydrogen from the acyl portion of the ester by t-butoxy radicals which result from the thermal decomposition of di-tertiary butyl peroxide. In one instance, this procedure was utilized to make a branched ester from hydrogen abstraction from the alcohol portion of the ester.

Experimental Procedures

Materials

Olefins. 1-Decene and 1-hexadecene obtained from the Gulf Oil Corporation were 99% and 93% pure respectively when examined by GLC. 3,7-Dimethyl-1-octene, 2,4,4-trimethyl-1-pentene (both 99% grade from the Chemical Samples Company) and 4-phenyl-1-butene, 3,5,5-trimethyl-1-hexene (both 95% grade from the Columbia Organic Chemicals Company) were used as received.

Initiators. Di-tertiary butyl peroxide was purchased from Monomer-Polymer Laboratories, and t-butylperoxy isopropyl carbonate from the Pittsburgh Plate Glass Company. Both of the initiators were used without further treatment.

Esters. Methyl stearate was made by refluxing a mixture of stearic acid (Hystrene 97% from the Humko Products Division of the National Dairy Products Corporation), excess absolute methanol, and catalyst (p-toluenesulfonic acid) for 16 hr. The product, twice crystallized from acetone 10:1, melted at 38–39C and was estimated to be 96.5% pure by GLC.

Methyl isostearate was prepared from isostearic acid obtained from Emery Industries Inc. The ester product, after preparation in the usual manner, was examined by GLC and was shown to contain some short-chain material. This was removed as a distillation fore-run (135C at 1.5 mm). The residue had a saponification equivalent of 299 (SE for methyl stearate is 298) and was used without further treatment.

Benzyl 2,2-dimethylpropanoate (benzyl pivalate) was prepared by reacting pivaloyl chloride with benzyl alcohol in pyridine. The resultant ester was purified by fractional distillation and was 98+% by GLC.

Addition Procedures

Generally the branched esters listed in Table I were made by the addition of the respective esters to the terminal olefin in the manner previously described (1,2).

In the preparation of α-hexadecylbenzyl 2,2-dimethylpropanoate it was necessary to resort to column chromatography in order to get material of sufficient quality for evaluation. The reaction mixture, after removal of the excess of benzyl pivalate by distillation, was first subjected to crystallization from Skelly B. The by-product hydrobenzoin bis-2,2-dimethylpropanoate separated out as a crystalline solid, mp 157–158C. The residue from the filtrate was chromatographed on a Florisil column to yield α-hexadecylbenzyl 2,2-dimethylpropanoate. The identity of the hydrobenzoin bis-2,2-dimethylpropanoate was established through its NMR and mass spectra and its saponification to yield hydrobenzoin which had proper IR spectrum, mp, and C & H analyses.

Testing Procedures

The esters were evaluated in three areas: kinematic viscosity and viscosity index, wear test, and thermal stability. The results of these evaluations are given in Tables II and III.

The viscosity and viscosity index were determined according to the procedures given in ASTM D445–60 and ASTM D567–53 respectively by using Cannon-Manning semimicro viscometers. The ASTM slope was derived according to D341–43.

Wear-test data were obtained by means of the Precision Shell Four-Ball Wear Test according to the procedure described by Peale et al. (5).

The thermal stability data were obtained by using an Aminco Thermograv instrument. The modifications of the instrument and the procedures employed were described by Parker (6).

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TABLE I

Preparation of Esters

Analysis					Analysis			
					C%		H%	
Product	Reactants	Yield[a] %	MP °C	n_d^{60}	Calc.	Found	Calc.	Found
Methyl 2-(3,7-dimethyloctyl)-octadecanoate	Methyl octadecanoate and 3,7-dimethyl-1-octene	42	13	1.4389	79.38	79.65	13.32	13.37
Methyl 2-(3,5,5-trimethylhexyl) octadecanoate	Methyl octadecanoate and 3,5,5-trimethyl-1-hexene	41	15	1.4358	79.18	79.37	13.29	13.18
1,3-(2,2-dimethylpropyl) bis-2-decyloctadecanoate	Methyl 2-decyloctadecanoate and 2,2-dimethylpropanediol		3	1.4474	79.84	80.14	13.18	13.07
Methyl 2-(4-phenylbutyl)-octadecanoate	Methyloctadecanoate and 4-phenyl-1-butene	43.5	34	1.4641	80.87	81.13	11.70	11.74
Benzyl 2-(4-phenylbutyl)-octadecanoate	Methyl 2-(4-phenylbutyl)-octadecanoate and benzyl alcohol		40	1.4862	82.95	82.86	10.74	10.75
α-Hexadecylbenzyl 2,2-dimethylpropanoate	Benzyl 2,2-dimethylpropanoate and 1-hexadecene	23	20	1.4600	80.71	81.24	11.61	11.49
Methyl 2-decylisostearate	Methyl isostearate and 1-decene	50	13	1.4425	....	....	....	....
Methyl 2-decyloctadecanoate[b]		54	37	1.4390	79.38	79.35	13.32	13.21

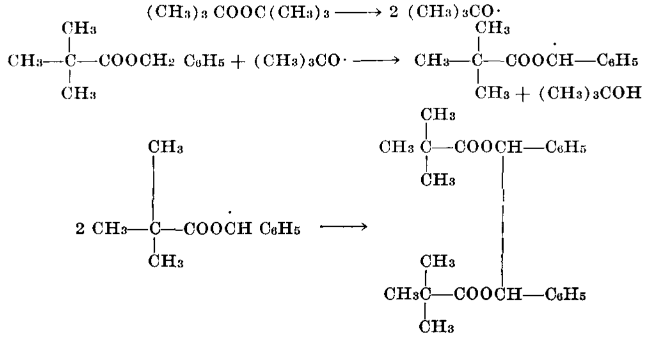
[a] Yield calculated from TLC results; where no yield is shown, ester interchange was method of preparation.
[b] Ref. 2.

Results and Discussion

The yields of esters given in Table I are based on olefin and are calculated from TLC prep plate data on samples taken from the crude reaction mixture after completion of the experiment.

As indicated in Table I, it was not possible to make methyl 2-(2,4,4-trimethylpentyl)octadecanoate. Attempts to add methyl octadecanoate to 2,4,4-trimethyl 1-pentene with either di-tertiary butyl peroxide or t-butylperoxy isopropyl carbonate (7) as free radical initiator were unsuccessful. The olefin in this instance has one of the branch methyl groups attached to the internal ethylenically bonded carbon atom. Since the addition of the esters takes place at the terminal carbon of the olefin, lack of success was unexpected. It appears that, with branching on the 2-carbon, steric influences were strong enough to hinder the addition of the ester.

Hydrobenzoin bis-2,2-dimethylpropanoate, obtained as a by-product in the preparation of α-hexadecylbenzyl 2,2-dimethylpropanoate, may be regarded as the dehydro-dimer of benzyl pivalate. In all probability it was formed by the following sequence of reactions:



$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2\ (CH_3)_3CO\cdot$$

$$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}COOCH_2\ C_6H_5 + (CH_3)_3CO\cdot \longrightarrow CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}COO\dot{C}H{-}C_6H_5 + (CH_3)_3COH$$

$$2\ CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}COO\dot{C}H\ C_6H_5 \longrightarrow \begin{array}{c} CH_3\underset{CH_3}{\overset{CH_3}{C}}{-}COOCH{-}C_6H_5 \\ | \\ CH_3\underset{CH_3}{\overset{CH_3}{C}}{-}COOCH{-}C_6H_5 \end{array}$$

The formation of this product can be considered as analogous to the formation of the dehydro-dimer which results from the reaction of methyl oleate and di-tertiary butyl peroxide as reported by Paschke and Wheeler (8). Their reaction product is an example of coupling at the 2-position by hydrogen abstraction from the carbon *alpha* to the carbomethoxy group. In the formation of the dehydro-dimer from benzyl pivalate this type of coupling is not possible. However it is possible to abstract a hydrogen from methylene of the benzyl group, and the resultant free radical is, by delocalization, strongly resonance-stabilized. Coupling of the radicals so formed yields the dehydro-dimer by-product.

The effect of branching in lowering the melting point of esters is well known. Multibranching within the branch has a similar effect, and this is ably demonstrated by comparing the melting points of the aliphatic esters in Table I with that of methyl 2-decyloctadecanoate. It will be observed that both methyl 2-(3,7-dimethyloctyl)octadecanoate and methyl 2-(3,5,5-trimethylhexyl)octadecanoate melt at least 20 degrees lower than methyl 2-decyloctadecanoate. Another noteworthy example of the effect of multiple branching is the diester 1,3-(2,2-dimethylpropyl) bis-2-decyloctadecanoate. This ester has a molecular weight of 917 and has a melting point 35 degrees lower than methyl stearate.

The data for thermal stability of the esters are given in Table II. The results provide additional evidence that blocking groups in the 2-position enhance the thermal stability of the esters. It will be noted also that the thermal stability of α-hexadecylbenzyl 2,2-dimethylpropanoate is rather low in spite of the presence of an aryl group in the alcohol portion of the ester. This result however is consistent with the view that the presence of β hydrogen in the alcohol portion permits facile formation of the 6-membered transition state (10) prior to decomposition. The replacement of a methylene hydrogen of the benzyl group by hexadecyl provided a source of β hydrogen.

Table III gives the data for the compounds evaluated as lubricants and lubricant additives. In general, the viscosity characteristics of the esters give VI values and ASTM slopes intermediate between the values for 100 paraffin-base mineral oil and DOS (di-2-ethylhexyl sebacate). The Shell-Boerlage Four-ball wear tests gave smaller wear-scars for the esters alone, but no significant improvement was observed

TABLE II

Thermal Stability of Esters

Ester	Onset of decomposition Temp. C	Temp. (°C) at which sample is decomposed approximately		
		1%	5%	10%
Methyl 2-(3,7-dimethyloctyl)-octadecanoate	360	380	402	420
Methyl 2-(3,5,5-trimethylhexyl)-octadecanoate	348	370	397	412
1,3-(2,2-dimethylpropyl) bis-2-decyloctadecanoate	365	380	407	425
Methyl 2-(4-phenylbutyl)-octadecanoate	365	385	407	420
Benzyl 2-(4-phenylbutyl)-octadecanoate	370	390	411	428
α-Hexadecylbenzyl 2,2-dimethylpropanoate	290	297	315	327
Methyl 2-decylisostearate	305	330	393	412
Methyl 2-decyloctadecanoate	340	360	404	414

TABLE III

Lubricant Test Data

Compound tested	Wear-Scar Dia. mm			Viscosity Index			ASTM Slope		
	as Base oil	as 5% Additive in		as Base oil	as 5% Additive in		Base oil	as 5% Additive in	
		DOS[a]	100 paraffin[b]		DOS	100 paraffin		DOS	100 paraffin
Methyl 2-(3,7-dimethyloctyl)-octadecanoate	0.628	0.898	0.810	134	148	75	0.711	0.711	0.789
Methyl 2-(3,5,5-trimethylhexyl)-octadecanoate	0.660	0.883	0.833	129	155	75	0.723	0.696	0.742
1,3-(2,2-dimethylpropyl) bis-2-decyloctadecanoate	0.553	0.847	0.715	154	157	80	0.620	0.697	0.780
Methyl 2-(4-phenylbutyl)-octadecanoate	0.638	0.877	0.765	126	147	77.5	0.704	0.706	0.820
Benzyl 2-(4-phenylbutyl)-octadecanoate	0.743	0.903	0.777	134	150	83	0.701	0.705	0.773
α-Hexadecylbenzyl 2,2-dimethylpropanoate	0.833	0.863	0.755	139	153	74	0.688	0.692	0.783
Methyl 2-decylisostearate	0.605	0.853	0.813	126	150	78	0.860	0.703	0.782
DOS	0.872	....	....	158	......	....	0.692	....	....
100 Paraffin	0.803	....	....	76	......	....	0.782	....	....

[a] DOS (di-2-ethylhexyl sebacate).

[b] 100 paraffin (Refined Pennsylvania oil with a viscosity of 100 saybolt seconds at 100F).

when the esters were used as additives to 100 paraffin-base mineral oil and DOS. One sample of methyl 2-decylisostearate was further tested as a base oil. The addition of 5% EOS (General Motors Engine Oil Supplement, containing zinc dialkyl dithiophosphate) and 5% TCP (tricresyl phosphate) to the isostearate improved the antiwear properties but not to the extent observed when the same materials were added to 100 paraffin-base mineral oil and DOS.

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