rates of incorporations of acetate into various fatty acids of liver separated by analytical GLC. Dietary differences have been shown to cause marked differences in these relative rates of uptake. The positive results gained in this investigation suggest further experiments of this nature.

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Potential Synthetic Lubricants: Esters of C_{18}-Saturated Cyclic Acids[1]

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Abstract

A series of 16 esters of C_{18}-saturated cyclic acids (HCal) were prepared, and partial evaluation showed that several have qualities that recommend them as potential low-temp lubricants. Starting materials used were primary, straight, and branched chain alcohols C_4–C_7; perfluoro alcohols; phenol; cyclohexanol; and C_{18}-saturated cyclic alcohols prepared from cyclic acids. Viscosities were measured at –40, 100, and 210F. Their viscosity indexes ranged from 26 to 143. Pour points or melting points of the esters ranged from –27 to –96F. The oxidative stability of these esters measured at 347F according to a modification of the test method for military specification MIL–L–7808 was in nearly all cases equal or superior to the control bis-2-ethylhexyl sebacate. More severe oxidation tests showed the esters of HCal to be slower than the control in the development of acidic decomposition products.

Introduction

AN INVESTIGATION of the derivatives of C_{18}-saturated cyclic acids was undertaken as a part of the program to find new and extended uses for linseed oil. The C_{18}-cyclic acids are derived from the linolenic component of linseed oil (12,16,17). The preparation and evaluation of cyclic acids and their derivatives have been described in earlier publications from this laboratory (4,6,7,11,14,15,18) including a review paper (9). Initially the hydrogenated C_{18} cyclic acids (HCal) and their derivatives appeared to show poor oxidative stability. It was later found that under certain conditions of "hydrogenation" HCal could contain significant quantities of an aromatic acid (5,10). Aromatic structures containing long alkyl side chains are known to be quite unstable to oxidation. Our recent work has demonstrated that HCal can be prepared free of aromatic acid, enabling us to investigate HCal esters as synthetic lubricants.

Ester lubricants, particularly dibasic acid esters, date back to World War II, when a lubricant was needed that combined low pour point, good stability, and high viscosity index in addition to having good lubricity. Mono- and diesters of organic acids were investigated and as a class of compounds proved to be promising. In the late 1940's, development of the gas turbine placed such severe requirements on lubricants that diesters became increasingly important. The development of the turbo-jet and the necessity of the military to operate under arctic conditions placed emphasis on low-temp properties and less on film strength. The requirements were set down in U.S. military specification MIL–L–7808 (1953).

Many synthetic lubricants have been tested on the basis of this specification. The most widely known of these are diesters of adipic, azelaic, and sebacic acids and glycol esters of pelargonic acid. Because of the cost of raw material and processing, sebacic acid is relatively high priced. The alcohols used in these diester lubricants are principally C_8–C_{10} oxo alcohols and 2-ethylhexanol. Branched chain alcohols are necessary to produce the desired low-temp viscosities. It is well known that the oxidative stability of alcohols containing tertiary hydrogens (branched chain alcohols) is less than that of their straight chain isomers. Thus the present dibasic acid ester lubricants are a compromise between low-temp fluidity or pour point and oxidative stability. In contrast to the dibasic acids, saturated C_{18}-cyclic acids have unique inherent low-temp properties; also their short straight-chain primary alcohol esters have good low-temp properties as well as superior high-temp oxidative stability as determined by formation of acidic products.

With the advent of the space age and new supersonic (mach 3) aircraft the search for better lubricating fluids has been intensified and now includes highly refined petroleum fractions, silicones, polynuclear aromatics, and fluoroesters, to name a few (1). Although the ester linkage lacks the stability required for many of these new applications, the need for good ester lubricants, particularly in subsonic aircraft, is expected to continue.

Preliminary evaluations of several esters prepared from HCal are reported in this paper. Some of these esters are of sufficient interest to warrant their further evaluation as potential lubricants.

Starting Materials

C_{18}-Saturated cyclic acids were prepared by alka-

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TABLE I
Viscosities and Pour Points of HCal Esters

Sample No.	Ester	Viscosity cs/sec			Viscosity index	Pour point, F
		100F	210F	−65F[a]		
1	HCal *n*-butyl	10.37	2.82	6,500	133	−96[b]
2	HCal *n*-pentyl	11.60	3.03	8,000	134	−69[b]
3	HCal *n*-hexyl	12.74	3.23	12,000	130	−49[b]
4	HCal *n*-heptyl	14.16	3.48	13,000	143	−27[b]
5	HCal 2-ethylbutyl	13.57	3.29	15,000	121	−88
6	HCal 2-ethylhexyl	16.30	3.66	29,000	126	−78
7	HCal 40% Aromatic 60% 2-ethylhexyl	15.69	3.53	36,000	120	
8	Aromatic 2-ethylhexyl	15.73	3.55	30,000	121	−70
9	HCal 2,2-dimethylpentyl	18.27	3.71	100,000	97	−79
10	HCal cyclohexyl	25.8	4.70	200,000	112	−65
11	HCal phenyl	19.3	3.80	150,000	92	−51
12	HCal C_{18}-cyclic alcohol	61.8	8.88	700,000	123	−56
13	HCal Ø' ethyl[c]	8.90	2.33	13,000	79	−88
14	HCal Ø' propyl	9.21	2.36	15,000	75	−87
15	HCal Ø' butyl	10.28	2.48	32,000	63	−87
16	HCal Ø' octyl	15.75	3.04	300,000	26	−13
17	Bis-2-ethylhexyl sebacate	12.50	3.30	7,800	154	
	Specification MIL–L–7808	>11	>3	<13.000		−75

[a] Extrapolated viscosity.
[b] Melting points.
[c] Abbreviated nomenclature for fluoro esters (13).

line isomerization of linseed oil in ethylene glycol according to the method of Eisenhauer et al. (6). Hydrogenation of the monmeric fatty acid was carried out in 50% glacial acetic acid (10) to eliminate contamination with aromatic acids. The bulk of the straight-chain saturated acids was removed by crystallization from acetone −50C followed by centrifuging. The liquid fraction contained about 8% straight chain isomers, which were removed by the urea inclusion technique. The hydrogenated cyclic acids (HCal) contained < 1% straight-chain saturates and < 1% aromatic acids. Neutralization equivalent was 283 and iodine value < 1.

HCal containing 60% aromtic acids was prepared by hydrogenation of the isomerized (cyclized) monomeric acids in the absence of acetic acid and with reduced agitation. Under such conditions the competing dehydrogenation (aromatization) reaction predominates (10). After removal of the straight-chain saturates, the liquid fraction was analyzed by gas-liquid chromatography (GLC), ultraviolet (UV), and nuclear magnetic resonance (NMR) and was estimated to contain 40% HCal and 60% aromatic acids. This isomer ratio is fortuitous, since the precise conditions under which various isomer ratios are produced have not been defined.

Aromatic acids of high purity were obtained as previously reported (2,10) by heating the isomerized (cyclized) monomeric acids with a Pd catalyst in the absence of hydrogen. Mild hydrogenation of the product saturates the straight-chain mono- and dieonic acids without affecting the aromatics. The straight-chain saturates are then removed by low-temp crystallization from acetone. By GLC analyses liquid aromatic acids contained only traces of HCal and straight-chain isomers. The neutralization equivalent of this fraction was 278.

Alcohols	*Grade*	*Source*
n-Butanol	White label	Eastman Kodak (19)
n-Pentanol	White label	Eastman Kodak (19)
n-Heptanol	White label	Eastman Kodak (19)
2-Ethylhexanol	Practical	Eastman Kodak (19)
n-Hexanol	Practical	Eastman Kodak (19)
2-Ethylbutanol	Practical	Eastman Kodak (19)
2,2-Dimethylpentanol	Research	Eastman Chemical Products
Cyclohexanol	Highest purity	Matheson Coleman and Bell
Phenol	Reagent	Baker
Perfluoroethanol	Research	Aldrich Chemical Company
Perfluoro-n-propanol	Research	Columbia Chemical Company
Perfluoro-n-butanol	Research	Columbia Chemical Company
Perfluoro-n-octanol	Research	Columbia Chemical Company
C_{18}-cyclic	—	Our preparation

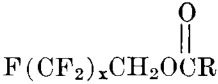
C_{18}-cyclic alcohols were prepared by chromite reduction (3) of the methyl esters of HCal. The distilled liquid product analyzed: 6.2% OH, acid value 0.5, and < 1.0% HCal methyl ester.

All these alcohols, except phenol and the C_{18}-cyclic alcohol, were distilled through a Podbielniak column (13 mm × 24 in.) packed with stainless steel Heli-Pac. The distillations were carried out at atmospheric pressure and with a 20:1 reflux ratio. A constant-boiling center cut was taken for esterification.

Preparation of Esters

The *n*-butyl, *n*-pentyl, *n*-hexyl, 2-heptyl, 2-ethylbutyl, 2-ethylhexyl, 2,2-dimethylpentyl, and cyclohexyl esters of HCal were prepared by heating together at about 70C for 1 hr, 1 part BF_3 etherate, 8 parts alcohol, and 4 parts HCal. The product was washed, extracted with petroleum ether, dried, and stripped of solvent and excess alcohol. Any acid present in the product was removed by passing it through a column packed with basic washed alumina. This ester was then distilled under high vacuum through a short Vigreux column. Any low-boiling material was removed in a small forerun and the remaining distillate collected for evaluation.

The perfluoro (ethyl, *n*-propyl, *n*-butyl, and *n*-octyl) esters of HCal were prepared by heating together equal parts of BF_3 etherate and HCal with a 10% molar deficiency of perfluoro alcohol. The symbol (Ø') will hereafter be used in referring to perfluoro esters with the generalized structure



$F(CF_2)_xCH_2O\overset{\overset{O}{\|}}{C}R$. An excess of acid was used because the alcohols were in short supply. This mixture was not completely miscible at room temp so the reaction was carried out at a temp 5 to 10C above the solution temp. Samples were taken periodically until an acid value of < 15 was obtained. After the reaction mixture was washed, extracted with petroleum ether, dried, and stripped of solvent, the crude product was distilled under high vacuum. A small forerun was discarded; the main fraction (fluoro ester) was collected; and the excess HCal, being higher boiling, remained as residue. Any trace of acid in the ester fraction was removed by treatment with alumina.

The hydrogenated cyclic alcohol ester of HCal (C_{36} ester) was prepared the same way as the fluoro esters except the reaction temp was 70C for 2 hr. The excess acid was removed by high vacuum distillation, the pot residue being the C_{36} ester. The residue was passed through alumina and activated charcoal to remove color bodies and the last traces of acid.

The phenyl ester of HCal, as well as the 2-ethylhexyl esters of pure C_{18} aromatic acids and the aromatic acids containing 40% HCal, was prepared by refluxing a 15:1 molar ratio alcohol:acid and about 3% fuming H_2SO_4 (based on the weight of the acid) with toluene. A trap was used to remove the water of esterification. The esters were isolated and purified as before. This method of esterification was used because BF_3-etherate led to large viscous undistillable residues when either the acid or the alcohol contained an aromatic ring.

Measurement of Viscosities

The viscosities of the esters were determined in Ostwald-Cannon-Fenske pipets (Table I). A water bath was controlled at 100 and 210F ± 0.1 degrees to immerse pipets for viscosity measurements. To measure the viscosity at −40F ± 0.3 degrees a modification of the apparatus described in a previous publication (8) was employed. The viscosities were plotted against temp on ASTM standard viscosity-temp charts for liquid petroleum products (D341). The extrapolated viscosities at –65F were determined from these plots. The viscosity indexes were obtained from viscosities at 100 and 210F by using ASTM Method D567–41.

Pour Point. Cooling equipment was not available for measuring pour points by the standard ASTM Method D97–47. To get an approximation, the esters were packed in solid carbon dioxide overnight. They were then placed in an air bath, and the air bath in turn was immersed in a Dewar flask containing isopropanol and solid carbon dioxide. The temp was allowed to rise at a rate of 2C/hr. The temp at which the surface of the sample would deform in 5 sec when tipped was arbitrarily called the pour point.

Oxidation at 175C. A modification of the standard test method was again employed because of a limited supply of the esters. A 10–g sample of ester containing 50 mg of phenothiazine (inhibitor) and 1 sq cm of 0.005 in. copper foil was placed in a 30 cc vial. Through a capillary tube inserted to the bottom of the vial, filtered compressed air was metered at the rate of 500 cc/hr for 72 hr. The sample was heated by immersing the vial in a stirred oil bath maintained at 175.5C ± 0.5C. After oxidation the sample was filtered to remove traces of solid material that had formed.

Oxidation at 260C. This test was designed to emphasize differences in oxidation stability not apparent in the less severe test. A 10–g sample of ester, 50 mg of phenothazine, and 1 sq cm of 0.005 in. copper foil were placed in a 50-ml stainless steel rocker bomb. The vessel was pressurized to 50 psi with oxygen, sealed, heated to 260C, and maintained at the temp for 5 hr. After cooling, the sample was filtered before determining its acid value and viscosity.

Discussion

The alkyl esters of HCal show oxidative stability (175C) equal to or better than bis-2-ethylhexyl sebacate in most of the samples tested (Table II). Contamination of HCal with its aromatic counterpart, Table II sample Nos. 7 and 8, produces poor oxidative stability. The phenyl ester of HCal, sample No. 11, is quite unstable to oxidation. The stability of the fluoro esters is not quite as clear cut. The Ø′ octyl ester, sample No. 16 is quite stable, but the Ø′ ethyl ester, sample No. 13, is not. The alkyl esters of HCal showed less corrision to copper (microscopic examination) than the bis-2-ethylhexyl sebacate although the weight loss of 2 sq cm of copper foil was negligible in either case. Severe oxidation (260C) also showed mixed trends. All the HCal alkyl esters tested were far superior to bis-2-ethylhexyl sebacate in the development of free acid; however, with the exception of the 2,2-dimethylpentyl ester, sample No. 9, all the HCal esters tested showed a larger viscosity increase than the sebacate. As determined by these two physical measurements, the apparent reversal in stability may be partly due to the different fragments produced by decomposition of these esters; i.e., the viscosity of the oxidized product could be affected by the nature of the fragments produced. Since these severe oxidation studies were single experiments and were not carried out on all esters, the accuracy of the reported data has not been established and individual values should be considered significant only as they apply in establishing a general trend.

TABLE II
Oxidative Stability of HCal Esters

Sample No.	Ester	Increase in acid value		% Increase in viscosity at 100F	
		175C	260C	175C	260C
1	HCal *n*-butyl	< 0.3		2.2	
2	HCal *n*-pentyl	< 0.3	21	2.0	21.0
3	HCal *n*-hexyl	< 0.5		2.4	
4	HCal *n*-heptyl	< 0.5	9	1.7	15.3
5	HCal 2-ethylbutyl	< 1.0	26	< 0.5	22.7
6	HCal 2-ethylhexyl	< 0.5	23	1.8	17.3
7	HCal 40% Aromatic 60% 2-ethylhexyl	12.3		57.8	
8	Aromatic 2-ethylhexyl	3[a]		18.0[a]	
9	HCal 2,2-dimethylpentyl	< 0.3	17	< 0.5	4.5
10	HCal cyclohexyl	< 0.3		< 0.5	
11	HCal phenyl	14.7		278	
12	HCal C_{18}-cyclic alcohol	< 1		4.7	
13	HCal Ø′ ethyl[b]	3.4		14.6	
14	HCal Ø′ propyl		38		47
15	HCal Ø′ butyl	1.1			
16	HCal Ø′ octyl	< 0.3		2.8	
17	Bis-2-ethylhexyl sebacate	< 0.5	37	3.0	11.2

[a] Oxidation in the absence of copper foil.
[b] Abbreviated nomenclature for fluoro esters (13).

The viscosities (VI's) and pour points are recorded in Table I. The VI's of the straight-chain alkyl esters range from 130 to 143, singly branched chain esters from 120–126, and the neopentyl structure, sample No. 9, 97. The Ø′ fluoro esters, sample Nos. 13–16, have poor VI's ranging from 26 for the Ø′ octyl ester to 79 for the Ø′ ethyl ester. The cyclohexyl ester, sample No. 10, had a VI of 112, whereas the phenyl ester, sample No. 11, which is quite unstable to oxidation, had a VI 20 units lower at 92. The C_{36}-ester prepared by condensing HCal alcohols with HCal, sample No. 12, had a VI of 123.

All the esters met the viscosity requirements (MIL–L–7808) at 100 and 210F except for the *n*-butyl ester, sample No. 1, and three of the fluoro esters, sample Nos. 13–15.

The extrapolated low-temp viscosities of the straight-chain alkyl esters all meet the requirements of the specification, but the pentyl, hexyl, and heptyl esters all crystallize above –75F. Most of the branched-chain alkyl esters and fluoro esters failed to meet the extrapolated low-temp viscosity requirement although exhibiting satisfactory pour points. These esters become increasingly viscous as they are cooled until they reach a point at which they form a clear glass, whereas the straight-chain alkyl esters remain quite fluid down to their freezing point.

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