Derivatives of Long Chain Fatty Acids as Lubricant Components[1]

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ABSTRACT

Soaps of *cis*-9,10-epiminostearic acid have been synthesized and tested as components of lubricating greases. The lithium, sodium and potassium soaps were obtained by the reaction of β-iodocarbamates with the proper alkali metal hydroxides in the ring closure step of the iodine isocyanate (INCO) procedure for the synthesis of internal aziridines. The soaps of other metals, namely barium, lead, aluminum and indium, were prepared from the alkali metal epiminostearates by metathetical reactions. As a result of this method of preparation, the aluminum and the indium soaps were isolated as the dicarboxylates rather than as the tricarboxylates. For the purpose of comparison a sample of lithium 9,10-epiminostearate was also prepared from the β-chlorocarbamate obtained by the addition of dichlorourethane (DCU) to methyl oleate. Since DCU addition is nonstereospecific, the soap obtained in this preparation was a mixture of *cis*- and *trans*-aziridines. Evaluation of the metal soaps as grease thickeners was made. The lithium derivative showed considerable promise as thickener having additional desirable properties.

INTRODUCTION

The present paper is part of a continuing program that is concerned with the conversion of long chain fatty acids to metal soaps for a study of their potential as lubricant components. Modifications and improvements in the design of aircraft and their engines have brought about many new requirements in lubricants. In an attempt to answer some of these demands, a variety of soaps of *cis*-9,10-epiminooctadecanoic acid were synthesized and tested as thickeners for lubricating greases. These soaps were prepared by the iodine isocyanate (INCO) addition to olefins procedure as originated by Drefahl et al. (1) in Germany and developed in this country by Hassner et al. (2) and by Swern et al. (3) and their respective students.

EXPERIMENTAL PROCEDURES

Methyl oleate was obtained from Applied Science Laboratories and had a purity of 99% by gas liquid chromatography (GLC). The inorganic chemicals were usual laboratory reagent grade, and they were used without any additional treatment.

The soaps prepared for the present study are listed in Table I. Sodium and lithium *cis*-9,10-epiminooctadecanoate were prepared from methyl threo-9(10)-iodo-10(9)-methylcarbamoyloctadecanoate (A) (2,3,4,5) by methods briefly outlined below.

Sodium *cis*-9,10-epiminooctadecanoate: To 236 g (0.47 mole) of the iodocarbamate (A) dissolved in 1420 ml of methanol was added 120 g (3.0 mole) of NaOH, and the mixture was refluxed overnight. The cooled reaction mixture was filtered, the filtrate (F) was reserved, and the precipitate on the funnel was extracted four times with 300 ml of hot methanol, and the residue, mostly sodium carbonate, was discarded. The methanol extracts were combined, evaporated to dryness, and the residue consisting, presumably, of the desired soap, sodium carbonate and sodium iodide, was washed three times with 200 ml of methanol to extract contained sodium iodide. The methanol washings were added to the original methanolic caustic filtrate (F) and the residue from these washings was taken up in 700 ml of hot methanol and any insoluble material (sodium carbonate) discarded. Evaporation of the methanol solution yielded 67.0 g of crude sodium soap, mp 217-220 C. To the alcoholic caustic filtrate (F) was added 1 liter of H_2O, and the methanol was boiled off on the steam bath. The resulting aqueous solution was allowed to cool overnight; the precipitated soap was filtered off and the filtrate discarded. The soap was washed with a small amount of cold water and dried. The dry soap, mp 216-219 C, weighed 70.5 g, giving a total yield of crude sodium soap of 137.5 g and equal to a 86.2% yield based on starting methyl oleate. The crude soap, recrystallized from 95% ethanol (1:6), gave 111.6 g of soap, mp 219-221 C, equal to a 70% yield based on starting methyl oleate. The estimated purity of the soap by titration (6) was 98.5%.

Lithium *cis*-9,10-epiminooctadecanoate: To 360 g (0.724 mole) of the iodocarbamate (A) in 2800 ml of methanol was added 168 g (4 mole) of lithium hydroxide monohydrate. The stirred mixture was refluxed for 11 hr and allowed to cool to room temperature. The solids were filtered off and the methanolic caustic filtrate (F) saved for work-up separately. The filter cake was washed with 750 ml of methanol. The washings were concentrated to one third volume and cooled to room temperature. A small amount of soap (5.9 g) separated out, was collected, and the filtrate was discarded. The filter cake, after being washed with 750 ml of water which was discarded, was successively extracted with: 2 liter, 1.5 liter, 1.5 liter, 1.5 liter and 0.5 liter of boiling 95% ethanol. The material remaining after the extractions, lithium carbonate, was discarded. Each extract was allowed to cool to room temperature, the separated soap filtered off, and the filtrate refrigerated at -30 C. The precipitated soap was filtered off, the filtrate concentrated to half its original volume and again refrigerated. The process was continued until no more soap was obtained as determined by taking a melting point of each precipitate. From all the extract fractions a total of 99.1 g of soap was obtained. The methanolic caustic solution (F) was concentrated to half volume and allowed to cool to room

TABLE I

Metal Soaps

Soap	mp, C	Estimated purity, %
$Na(C_{18}H_{34}NO_2)$[a]	219-221	98.5
$Li(C_{18}H_{34}NO_2)$	201-207	98.7
$Ba(C_{18}H_{34}NO_2)_2$	164-166	99.5
$Pb(C_{18}H_{34}NO_2)_2$	87.95	99.7
$In(OH)(C_{18}H_{34}NO_2)_2$	77-86	98.3
$Al(OH)(C_{18}H_{34}NO_2)_2$	126-132	96.8

[a] $(C_{18}H_{34}NO_2)$ = *cis*-9,10-Epiminooctadecanoate Anion.

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[1] Presented at the AOCS-ISF World Congress, Chicago, September 1970.

[2] E. Market. Nutr. Res. Div. ARS, USDA.

TABLE II

Grease Performance Tests

Test	Lithium *cis*-9-10-epiminooctadecanoate grease[a]			Lithium 12-hydroxystearate grease[b]
	Diester oil	Paraffin oil[c]	Silicone oil	Diester oil
Unworked penetration	193	305	320	
Worked penetration	262	320	332	264
Dropping point, F	354	400	396	378
4-Ball extreme pressure	126 kg weld			
Bearing protection	Passes			
High temperature performance	250 F 1167 hr			1206 hr
Bomb oxidation	500 hr 50 psi loss			

[a] All at 15% concentration; no additives incorporated into grease sample.

[b] Contains 16.2% soap with 2.5% anti-oxidant as an additive.

[c] Designated as Grade 1100 according to Military Specifications Mil-L-6082C.

temperature. The separated soap was filtered off and washed with a small amount of water to remove any contaminating lithium iodide and caustic. Both water washings and filtrate were discarded. The amount of soap obtained here was 20.9 g raising the total amount of soap obtained to 125.9 g, equal to a 55.4% yield of soap based on starting carbamate. A portion of this soap was recrystallized from 95% ethanol. It then melted at 201-207 C.

Barium *cis*-9,10-epiminooctadecanoate: To a hot solution of 41.66 g (0.13 mole) of sodium *cis*-9,10-epiminooctadecanoate in 1250 ml of H_2O was slowly added, with stirring, a hot solution of 31.86 g (0.13 mole) of $BaCl_2 \cdot 2H_2O$ in 320 ml of H_2O. Stirring was continued until the mixture cooled to room temperature, after which the mixture was allowed to settle overnight. The precipitated soap was water-washed until the washings were shown to be free of chloride ion and then dried. The weight of soap was 47.0 g, and the yield was essentially quantitative.

Lead *cis*-9,10-epiminooctadecanoate: Thirty-two grams of 98.9% pure (by ash determination) sodium *cis*-9,10-epiminooctadecanoate (0.099 mole) were dissolved in 2.5 liter of water by heating; the solution was allowed to cool to 40 C and then filtered through a fritted glass funnel. To the stirred filtrate was added, in a dropwise manner, 32.8 gm (0.099 mole) of $Pb(NO_3)_2$ in 500 ml of water. Addition required 45 min, and stirring was continued for 30 min after the addition was completed. The mixture was allowed to settle overnight. The precipitate was washed by decantation until the filtered washings were free of lead ion by test with sodium sulfide solution. The dried soap weighed 39.6 g indicating a quantitative recovery.

Indium hydroxy-di-(*cis*-9,10-epiminooctadecanoate): This soap was prepared according to procedures described for similar aluminum soaps by Rakowitz (7). To a solution of 16.08 g (0.05 mole) of sodium *cis*-9,10-epiminooctadecanoate in 960 ml of H_2O was added 250 ml of 0.1N NaOH. The stirred solution was heated to 40 C and maintained at that temperature while 90 ml of a solution of 7.37 g (0.033 mole) of $InCl_3$ in 100 ml of H_2O was added in a dropwise manner. The addition of the $InCl_3$ solution was monitored by pH measurements and when the pH of the stirred mixture dropped to 6.0 the addition of $InCl_3$ was stopped. When the pH of the mixture remained constant for 30 min no more $InCl_3$ was added. The addition took place intermittently over a 24 hr period; heating and stirring was maintained throughout the period. The mixture was allowed to cool to room temperature, and the precipitated soap was filtered, washed and dried. The weight of soap was 17.65 g indicating a 97.4% of theory recovery.

TABLE III

Characteristics of Grease Made From Diester Oil and Lithium Soap Containing 2.5% PAN[a]

Test		After 2 weeks	After 2 months
Unworked penetration	212	257	253
Worked penetration	257	313	324
Dropping point	357 F		
Bomb oxidation	500 hr 5 psi loss		

[a] N-Phenyl-α-Naphthylamine as antioxidant.

Aluminum hydroxy-di-(*cis*-9,10-epiminooctadecanoate): To 16.08 g (0.05 mole) of the sodium soap was added 80 ml of 0.1N NaOH. The stirred solution was maintained at 40 C while 70 ml of an aluminum chloride solution, 0.033 mole of $AlCl_3 \cdot 6H_2O$ in 100 ml of H_2O, was added in a dropwise manner. The addition of $AlCl_3$ solution was monitored by pH measurements, and when the pH of the stirred mixture dropped to 6.0 the addition of $AlCl_3$ was halted. When the pH was constant for 30 min no more $AlCl_3$ was added. The collected soap was dried and amounted to 13.1 g. Owing to some mechanical losses in the first stage of the preparation, this amount of soap does not represent a true potential recovery. The theoretical yield of soap was 15.92 g.

Elemental analytical data were obtained for all the soaps but the aluminum soap, and the values obtained were in accord with those calculated from theory. In each instance, including the aluminum soap, estimations of purity were made from metal content determinations employing ashing techniques. These consisted of: ashing the soaps after they were heated with concentrated sulfuric acid; weighing the residue as metal sulfate for the sodium, lithium, barium and lead soaps and as the oxide for the indium and aluminum soaps. In a few cases it was possible to estimate purity by a titration procedure developed at this laboratory (6). All of the analytical data obtained supported the formulas for the respective soaps shown in the table.

For the greases the unworked and worked penetration, dropping point, 4-ball extreme pressure, bearing protection (rust preventive property), and bomb oxidation tests were made according to the procedures given in ASTM D1403, ASTM D2265, ASTM D2596-67T, ASTM D1743 and ASTM D942-50, respectively. The high temperature bearing performance test was carried out as given in Federal Test Method Standard No. 791B, Method 331. For evaluating the oil additives with regard to wear scar the Precision-Shell 4-ball wear test was used. The samples were run at 120 C under 50 kg load for 1 hr as described by Peale et al. (8). The rotation of the upper ball was 600 rpm.

RESULTS AND DISCUSSION

Only the alkali metal soaps were prepared by reaction between the iodocarbamate and alcoholic caustic. In the preparation of these soaps, because of the difference in the solubility of the soaps themselves and the metal carbonates,

TABLE IV

Wear and Extreme Pressure Tests

Base oil	Additive	Ave. wear scar, mm	Extreme pressure test, weld point kg
100 Paraffin oil	None	0.803	120
100 Paraffin oil	5% Li Soap[a]	0.796	140
100 Paraffin oil	5% Me Ester[b]	0.807	120
Diester oil	None	0.872	100
Diester oil	5% Li Soap	0.907	150
Diester oil	5% Me Ester	0.765	120

[a] Li Soap = Lithium *cis*-9,10-Epiminooctadecanoate.

[b] Me Ester = Methyl *cis*-9,10-Epiminooctadecanoate.

no single procedure was totally applicable to their preparation. The other soaps were prepared by metathesis from solutions of the sodium soap and the appropriate metal ion. The soaps of the monovalent and divalent metals were obtained as normal soaps. The indium and aluminum derivatives were obtained as dicarboxylates. It was not possible to prepare the soaps directly from the free acid because of the instability of the carboxylic acid. The internal aziridine ring is susceptible to scission by nucleophilic attack of carboxylic acids (4,9,10).

Recently Foglia et al. (4) have reviewed the stereochemical routes of INCO and N,N-dichlorourethane (DCU) additions to methyl oleate in the synthesis of epiminostearates. The stereospecificity of the INCO addition was confirmed. From this information it is known that all of the epimino soaps in Table I have the same geometrical configuration as the starting methyl ester. For comparison purposes a sample of lithium 9,10-epiminooctadecanoate was also prepared by the addition of DCU to methyl oleate. The investigators quoted above have shown that DCU additions are free radical in behavior as opposed to INCO additions which are ionic. Consequently, the DCU addition being nonstereospecific, the soap obtained was a mixture of *cis*- and *trans*- aziridines.

There is a marked difference in the water solubility of the *cis* and *trans* lithium aziridine soaps. At room temperature a saturated solution of lithium *cis*-9,10-epiminooctadecanoate contains about 0.12% of soap. On the other hand the *trans* soap is about 40 times more soluble. This difference in solubility is of great significance when the soap is to be used as a constituent of a grease that may be exposed to water.

The soaps were evaluated as grease thickeners and under the conditions tried only the lithium soap produced a stable grease. However further work is planned toward finding suitable procedures for making stable greases with the other soaps. Three different types of oils, a hydrocarbon oil, a diester and a silicone fluid, were made into greases using lithium *cis*-9,10-epiminooctadecanoate as the thickener. Table II shows the results of tests made on the greases.

The mechanical stability of a lubricating grease is very important in its use. The penetration value is a measure of the softness or hardness of a grease and of the relative changes in this characteristic after being subjected to a limited amount of mechanical shear. Two of the three greases, although somewhat soft to start with, retained good consistency after working. The larger change in the diester-based grease after being subjected to shear is not unexpected, as this is a characteristic of lithium diester greases (11,12) and is generally compensated for by the addition of 1% of a structural modifier such as a polybutene (13). Typical lithium greases, often thickened with 12-hydroxystearate, have dropping points in the range between 350-400 F. All three of the epiminostearate grease samples have dropping points within this range.

The remaining tests in the table were applied only to the diester-based grease. The low weld point obtained with the grease indicates it to be unsuitable for use where high pressures are involved. The bearing protection test method that was applied to the sample is based on techniques which show correlation between laboratory results and service for grease-lubricated aircraft wheel bearings. Ordinarily a grease to pass this test requires the addition of a corrosion preventative. The epiminostearate-thickened grease passed the test without the use of an additive, an unusual property. The grease also proved to be suitable for lubricating lightly loaded bearings at high speeds and elevated temperatures by exceeding the 1000 hr at 250 F requirement in the high temperature performance test. Resistance to oxidation is measured by the bomb oxidation test. The magnitude of the oxygen pressure drop indicates inadequate oxidation inhibition without additive, but further tests are required to confirm this.

Table III lists the properties of a grease prepared from lithium *cis*-9,10-epiminostearate and diester oil and containing 2.5% of N-phenyl-α-naphthylamine (PAN) as antioxidant. The grease samples had acceptable stability characteristics over the stored period. The resistance to oxidation of the grease improved tenfold as a result of the incorporation of the additive. However this level of anti-oxidant addition concentration is far in excess of the amount required to give the necessary improvement in this property.

The lithium epimino soap and, for comparison purposes, the corresponding methyl ester were tested as oil additives and the results are reported in Table IV.

A 100 paraffin oil and diester oil were the base oils used in the evaluation. The results indicate no enhancement of either the wear or extreme pressure properties of the oils.

Although these derivatives contributed little as oil additives, the soap does have advantages as a grease thickener. Lithium *cis*-9,10-epiminooctadecanoate, when used as a thickener, contributed rust inhibitive properties to the grease without the use of additives. The problems of processing as well as the incompatibility factor are significantly reduced by having a thickener component with multiple properties.

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