Lubricants and Lubricant Additives: II. Performance Characteristics of Some Substituted Fatty Acid Esters

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ABSTRACT

Sixty-one compounds, principally substituted fatty esters of mono- and polyhydric alcohols, but including some amides and two imidazolidines, were prepared and evaluated as lubricants and lubricant additives for paraffin and diester base oils. The effects of chloro, phosphato, phosphorodithio, thio, epithio, mercapto, and sulfuryl substituents, alone and in certain combinations, on the performances of the compounds as antiwear and extreme pressure lubricants were investigated. The epithio (thiirane) group was the most effective and consistent in enhancing extreme pressure and antiwear performances of the compounds as additives. Sulfurized and chloro-sulfone derivatives also were effective, but perhaps somewhat less predictably so, than the epithio derivatives. The phosphato and phosphorodithio derivatives were good, consistent, antiwear additives, but only the latter seemed potentially useful for improving extreme pressure lubrication. Structure-performance correlations favor use of the esters over the amides.

INTRODUCTION

The embargo on the importation of sperm whale oil and its products into the US has spurred intensive search for satisfactory substitutes. Required are lubricants, particularly as antiwear and extreme pressure (EP) additives. An obvious substitute for sperm oil would be a closely similar synthetic composition of esterified fatty alcohols and acids. Such a substitute has been shown to be feasible technically (1), but perhaps too expensive (2). A simpler substitute of perhaps one or two fatty ester derivatives, whose chain lengths and unsaturation equal, on the average, those of the natural product, might be better cost performancewise. Many N-mono- and N,N-disubstituted amides of fatty acids containing one or more thiirane groups are good extreme pressure lubricants and effective antiwear and extreme pressure additives for paraffin or diester base lubricants, and occasionally for both (3). Incidental and cursory data have indicated that similar derivatives of fatty acid esters might perform even better in such roles and be suitable replacements for sperm oil derivatives. We, therefore, prepared and evaluated a series of substituted stearates of various mono- and polyhydric alcohols.

We report the results of these studies and those of additional amide derivatives investigated since our last report (3).

EXPERIMENTAL PROCEDURES

None of the compounds prepared and evaluated were of high purity. They received minimum purification, usually acid or alkaline washes followed, where advisable, by percolation through activated alumina to eliminate any residual acidity. Thus, the actual elemental analyses often differed from the calculated values.

All but the disubstituted *trans* and tetrasubstituted stearic acid derivatives were prepared from commercially available materials. Oleic acid, Elaine 233LL (Emery Industries) was the precursor of all but one of the 9,10-substituted stearic acid derivatives.

The disubstituted *trans* derivative was derived from purified elaidic acid, and the tetrasubstituted derivatives were from a 90-95% in-house preparation of linoleic acid, which had been obtained from safflower fatty acids by urea clathration (4).

Ester intermediates were prepared, except as noted, by the direct reaction between the alcohols and fatty acids with 3.0 g of *p*-toluenesulfonic acid per 100 g of fatty acid as catalyst. The relative ease of reactant removal dictated whether a slight excess of alcohol or fatty acid was employed in a specific preparation.

Ester-amide intermediates were prepared by the reaction at reflux of alkanolamine and fatty acid in a Dean-Stark apparatus in the presence of an entrainer, benzene. Amides were prepared as reported previously (3).

Imidazolidine intermediates were prepared as reported by Mod, et al., (5).

Preparations

2,3-Epithiopropyl 9,10-epithiostearate. The glycidyl oleate (2,3-epoxypropyl oleate) intermediate required was prepared by the nonaqueous "Method A" of Maerker, et al., (6); and 120 g (0.35 mole) of the glycidyl oleate, oxirane content 4.04% (theory 4.70%), then was epoxidized at 25 C by the addition, with stirring, of 72.0 g (0.41 mole) of *m*-chloroperbenzoic acid in 800 ml of $CHCl_3$. The recovered 2,3-epoxypropyl 9,10-epoxystearate had an oxirane content of 7.98% (theory 9.03%).

One hundred twenty-five g (0.35 mole) of 2,3-epoxypropyl 9,10-epoxystearate in 300 ml of dioxane was added to an aqueous solution of thiourea (53.6 g, 0.70 mole) in minimal water and 113.3 g (0.35 mole) of 30% sulfuric acid following the procedure and workup reported previously (3). This preparation was analyzed as 8.30% sulfur (theory), 12.94%) and did not polymerize. Preparations of the compound with sulfur content of 8.35% or more polymerized during storage.

0,0-Dialkylphosphorodithioic Acid Derivatives

0,0-Dibutylphosphorodithioic Acid (I). One mole of P_2S_5 was added slowly to 4 moles of vigorously stirred n-butanol at 60-70 C, according to Martin, et al., (7). The crude product was purified as reported by Bacon and LeSuer (8), except for omission of the fractional distillation step. It was an unpleasant smelling apple green liquid.

N-[9(10)-0,0-Dibutylphosphorodithio]stearoylmorpholine. Thirty-one g (0.13 mole) of I and 45 g (0.13 mole) of oleoymorpholine were heated at 70-80 C, with stirring, under nitrogen for 6 hr. Unreacted I was removed from an ether solution of the reaction product with 100 ml of 10% aqueous sodium bicarbonate. The ether layer was separated, washed with water, dried over anhydrous sodium sulfate, and stripped. Analysis of the product (phosphorous, 1.21%; theory, 5.22%) showed that only ca. one-fifth of the desired double bond addition had occurred.

The addition of 0,0-dialkylphosphorodithioic acid to an internal double bond as found in monoolefinic fatty acids, such as oleic, did not proceed readily as did the additions to terminal olefins reported by Bacon and LeSuer (8). The extent of the reaction with a nonterminal double bond in our work ranged from ca. 23% for a 9,10-octadecenoic acid

TABLE I

Wear and Extreme Pressure Lubricating Characteristics of Some Esters and Amides of Substituted Fatty Acids

Sample Number	Compound	Scar Diameter mm			Extreme Pressure Tests						
					Neat			5% in Base Oil			
			5% Additive in					Weld Pt(kg)		Scar Dia(mm) *	
		Neat[a]	Topaz	DOS	Load(kg)	Scar(mm)	Weld Pt (kg)	Topaz	DOS	Topaz	DOS
1	2-Ethylhexyl epithiostearate	0.555	0.675	0.678	---	---	520	180	200	4.10	3.70
2	2-Ethylhexyl epithiotallate	0.710	0.410	0.452	520	3.15	540	190	190	2.85	3.15
3	2-Ethoxyethyl 9,10-epithiostearate	---	0.480	0.478	---	---	---	160	250	2.68	2.99
4	2-(2-Ethoxyethoxy)ethyl 9,10-epithiostearate	---	0.462	0.447	---	---	---	150	170	3.17	2.72
5	4-Methoxyphenyl 9,10-epithiostearate	---	0.703	0.907	---	---	---	210	200	3.78	3.35
6	2-Ethoxyphenyl 9,10-epithiostearate	---	0.695	0.483	---	---	---	160	170	2.75	2.62
7	2-Ethoxyethyl 9,10,12,13-diepithiostearate	1.01	0.573	0.598	480	3.25C	500	190	220	3.42	2.89
8	2-(2-Ethoxyethoxy)ethyl 9,10,12,13-diepithiostearate	0.99	0.535	0.530	600	3.05	b/	220	210	3.00	3.05
9	Methyl(2,3-epithiocyclohexyl) 9,10-epithiostearate	---	0.690	0.553	---	---	---	220	240	2.70	3.10
10	1,2-di(9,10-Epithiostearoyloxy)ethane	0.608	0.715	0.680	320	3.18	340	160	160	2.85	3.25
11	2,2'-Oxydiethyl bis-(9,10-epithiostearate)	0.573	0.435	0.437	600	2.70	b/	220	210	3.80	3.27
12	1,4-bis(9,10-Epithiostearoyloxy)-2-butene	---	0.775	0.450	---	---	---	220	240	3.10	3.30
13	1,3-bis(9,10-Epithiostearoyloxy)propane	0.910	0.617	0.902	390	3.47CL	400	170	190	2.72	3.18
14	9,10-Epithiostearoyl terminated sebacic acid--1,3-propanediol polyester	---	0.925	0.715	---	---	---	190	210	3.01	3.86
15	Pentaerythrityl tetra(9,10-epithiostearate)	---	0.475	0.475	---	---	---	200	240	3.61	3.90
16	1,2-bis(9,10,12,13-Diepithiostearoyloxy)ethane	0.650C	0.538	0.515	600	2.21MC	b/	230	220	3.08	3.05
17	2,3-Epithiopropyl 9,10-epithiostearate	---	0.605	0.765	---	---	---	180	200	2.85	3.55
18	9,10-Epithiostearyl 9,10-epithiostearate	0.675	0.622	0.455	300	3.77	310	290	300	3.85	2.89
19	9,10-Epithiostearyl 9,10,12,13-diepithiostearate	0.795	0.543	0.455	600	2.30	b/	210	230	3.30	3.30
20	Epithioated soybean oil	0.597	0.492	0.548	500	2.15	c/	190	300	2.67	2.78
21	Epithioated jojoba oil	0.698	0.433	0.435	600	1.97	b/	210	210	2.92	2.83
22	Sulfurized 2-(2-ethoxyethoxy)ethyl oleate	0.527	0.620	0.529	530	3.55	540	200	220	3.27	2.89
23	Sulfurized cottonseed oil	0.800	0.480	0.875	600	1.95	b/	260	260	2.95	3.00
24	bis[2-(9,10-Epithiostearoyloxy)ethyl] sulfone	0.582	0.433	0.462	450	2.97	460	190	210	2.60	2.97
25	bis 2-(9,10,12,13-Diepithiostearoyloxyethyl)sulfone	0.615C	0.510	0.528	600	2.15C	b/	220	200	3.15	3.45
26	2-Ethoxyethyl 9(10)-hydroxy-10(9)-dibutylphosphatostearate	0.553	0.423	0.582	180	3.23	200	120	130	2.95	3.95
27	2-(2-Ethoxyethoxy)ethyl 9(10)-hydroxy-10(9)-dibutylphosphato-stearate	0.685	0.607	0.618	160	3.34	180	120	120	3.10	2.95
28	1,2-bis-[9(10)-Hydroxy-(10)9-dibutylphosphatostearoyloxy] ethane	0.640C	0.545	0.400	480	2.37CL	500	180	190	2.63	3.00
29	2-Ethoxyethyl[9,(10)-mercapto-(9)10-dibutylphosphato] stearate	0.515	0.610	0.460	380	2.62	400	160	160	2.60	2.97
30	1,2-bis[9(10)-Mercapto-(9)10-dibutylphosphatostearoyloxy]ethane	0.925	0.470	0.500	---	c	480	200	200	3.72	3.82
31	Phosphorylated 2-ethylhexyl epoxytallate	0.545	0.588	0.513	220	2.87	240	140	150	3.45	2.95
32	Phosphorylated epoxysoybean oil	0.612	0.873	0.560	500	2.24	600	170	170	2.65	3.05
33	2-Ethylhexyl x-hydroxy-y-(0,0-dibutylphosphorodithio)tallate	0.560	0.607	0.540	---	---	280	220	200	4.02	3.78
34	1,2,3-tris-Carbobutoxy-2(3)-(dioleyl phosphorodithio)propane	0.453	0.530	0.407	---	---	360	220	220	3.96	4.15
35	(3-Acetylthiopropyl) 9(10)-acetylthiostearate	0.730	0.815	0.983	---	---	320	180	200	4.03	3.85
36	2-(2-Ethoxyethoxy)ethyl 9(10)-(carbobutoxymethythio)stearate	0.695	0.653	0.922	---	---	220	180	180	3.90	4.20
37	2-Ethoxyethyl pentachlorostearate	1.47C	0.515	0.588	600	1.86	b/	200	140	3.30	3.65
39	2(2-Ethoxyethoxy)ethyl pentachlorostearate	1.12C	0.903	0.613	280	2.89	300	150	170	4.15	4.00
40	1,2-bis(Pentachlorostearoyloxy)ethane	0.910	0.900	0.905	500	1.53	540	260	200	2.90	3.03
41	2,2'-Oxy-bis-(ethyl pentachlorostearate)	1.03	0.980	0.915	600	1.82	b/	250	220	3.20	3.25
42	9,10-Epithiostearyl pentachlorostearate	---	0.708	0.718	---	---	---	230	210	2.67	3.40
43	2,2'-Thio-bis-(ethyl pentachlorostearate)	0.945	0.965	0.945	600	1.65	b/	200	200	2.90	2.85
44	bis[2-(Pentachlorostearoyloxy)ethyl]sulfone	0.750	0.983	1.11	---	c	520	320	260	3.95	3.70
45	9(10)-Hydroxy-10(9)-dibutylphosphatostearyl pentachlorostearate	0.605	0.588	0.710	340	2.87	360	200	180	3.35	2.93
46	{1 pt-Epithiostearyl epithiostearate; 1 pt-N-3(2-Ethoxyethoxy)propyl diepithiostearamide}	0.585C	0.420	0.425	600	2.15C	b/	200	200	3.00	2.70
47	{1 part 9,10-Epithiostearyl 9,10-epithiostearate; 1 part 9,10,12,13-Diepithiostearoylmorpholine}	0.750	0.530	0.447	600	2.73	b/	200	250	2.95	2.25
48	N-3(2-Ethoxyethoxy)propyl-9,10,12,13-diepithiostearamide	0.665	0.608	0.751	500	2.40	c/	170	220	2.90	3.38
49	N,N'-bis(9,10-Epithiostearoyl)polyoxypropylenediamine	0.536	0.418	0.430	600	2.23	b/	230	230	3.65	3.02
50	N,N'-Ethylene-bis-9(10)-hydroxy-10(9)dibutylphosphatostearamide	0.585	insol	0.418	---	---	---	insol	180	insol	3.30
51	N-Pentachlorostearoylmorpholine	1.15	1.12	1.00	160	2.35	---	200	180	3.20	2.85
52	N-(9-10-trans-Epithiostearoyl)morpholine	0.448	0.788	1.00	600	2.47	b/	200	200	3.25	2.85
53	N-[12-(9,10-Epithiostearoyloxy)-9,10-epithiostearoyl]morpholine	0.615	0.415	0.935	600	2.25	b/	190	210	2.95	3.05
54	Sulfurized morpholide of conjugated linoleic acid	0.758	0.570	0.828	460	3.35	500	190	180	3.25	2.90
55	9(10)-(Carbobutoxymethylthio)stearoylmorpholine	0.770	0.827	0.950	---	---	300	180	180	4.00	3.85
56	N-[9,10-(12,13)-Hydroxydibutylphosphato-9,10-(12,13)-epithiostearoyl]morpholine	0.625	0.645	0.532	340	3.75	350	200	160	3.15	3.25
57	N-[Phosphorylated(9,10,12,13-diepoxystearoyl)]morpholine	0.677	0.414	0.535	360	3.75	370	200	160	2.35	2.78
58	N-(9(10)-0,0-Dibutylphosphorodithio)stearoylmorpholine	0.695	0.750	0.457	---	c	340	180	180	3.95	4.62
59	N-[9(10)-Hydroxy-(9)10-(0,0-dibutylphosphorodithio)stearoyl] morpholine	0.800	0.503	0.453	---	c	300	200	180	4.20	4.17
60	Phosphorylated epoxystearoyl morpholine	0.555	0.520	0.682	240	3.25	260	150	160	3.02	3.33
61	1,3-bis-(9,10-Epithiostearoyl)imidazolidine	---	0.492	0.635	---	---	---	290	260	2.68	3.14
62	1,3-bis(Diepithiostearoyl)imidazolidine	0.445	0.640	---	---	---	320	220	insol	3.90	insol
CONTROL	Topaz 105 sec oil	0.794	---	---	---	---	120	---	---	---	---
CONTROL	Di 2-ethylhexyl sebacate	0.872	---	---	---	---	110	---	---	---	---
CONTROL	Gulfpride, Single G. multiviscosity	0.447	---	---	---	---	190	---	---	---	---
CONTROL	SAE #90 comm hypoid fluid	0.370	---	---	---	2.60	280	---	---	---	---

[a]Ball condition C=corroded, LC=light corrosion, MC-moderate corrosion, CL=corrosion at high loading.

[b]Beyond capacity of 4-ball tester.

[c]Test stopped, excessive fuming or decomposition.

*At highest nonwelding load.

derivative sample 58 to > 90% for an activated nonterminal double bond in a 1,2,3-tris(carbobutoxy)propene derivative (sample 34).

N - [9(10)-Hydroxy-(9)10-(0,0-dibutylphosphorodithio)-stearoyl]morpholine. Thirty g (0.12 mole) of I was added dropwise to 45.5 g (0.12 mole) of stirred 9,10-epoxystearoylmorpholine under nitrogen; the reaction was moderately exothermic. The mixture was heated at 60 C and stirred for an additional hour. It was cooled, dissolved in diethyl ether, washed with 100 ml of 10% aqueous sodium bicarbonate, washed with water, dried, and stripped. The reaction was 94-98% complete, based on the phosphorus and sulfur content of the product.

1,2,3-Tris(carbobutoxy)-2(3)-(dioleylphosphorodithio)propane. 0,0-Dioleylphosphorodithioic acid (35.2 g, 0.056 mole) was added dropwise to 19.1 g (0.056 mole) of stirred 1,2,3-tris(carbobutoxy)propene (tri-*n*-butyl aconitate) at 60-70 C; heating and stirring were maintained for 6 hr. The cooled reaction mixture was dissolved in diethyl ether, washed with 25 ml each of 10% NaOH and water, then dried and stripped. The phosphorus and sulfur analyses showed a 96-97% addition of the 0,0-dioleylphosphorodithioic acid to the activated double bond.

Lubricant Evaluation Test Procedures

Scar diameters were determined by use of a Precision

TABLE II

Estimated Purity of Preparation

Sample number	Estimated % of active component in sample[a]	Physical state of sample	Polymerizes[b]	Conditions[c]
1	71	liquid	no	----
2	68	liquid	no	----
3	67	liquid	no	----
4	44	liquid	no	----
5	62	liquid	no	----
6	68	liquid	no	----
7	68	liquid	no	----
8	77	liquid	no	----
9	61	liquid	yes	>90
10	59	liquid	no	----
11	83	liquid	yes	EP test
12	94	liquid	yes	90-120
13	67	liquid	no	---
14	25	viscous liquid	no	----
15	68	liquid	yes	170-180
16	49	liquid	no	---
17	64	liquid	yes	30-90
18	83	liquid	yes	180-300
19	66	liquid	yes	180-300
20	48	liquid	yes	60-90
21	33	liquid	no	----
22	100	liquid	no	----
23	100	liquid	no	----
24	63	liquid	no	----
25	27	very viscous	no	----
26	92	liquid	---	----
27	88	liquid	---	----
28	89	liquid	---	----
30	32	liquid	---	----
31	87	liquid	---	----
32	57	very viscous liquid	---	----
33	80	liquid	---	----
34	96	liquid	---	----
35	100	liquid	---	----
36	87	liquid	---	----
37	89	liquid	---	----
39	100	liquid	---	----
40	94	liquid	---	----
41	97	liquid	---	----
42	73	liquid	no	----
43	92	liquid	---	----
44	93	liquid	---	----
45	89	liquid	---	----
48	80	liquid	---	----
49	80	liquid	no	----
50	81	very viscous liquid	---	----
51	94	liquid	---	----
52	77	liquid	no	----
53	57	liquid	yes	180-300
54	100	liquid	---	----
55	87	liquid	---	----
56	20	liquid	---	----
57	71	liquid	---	----
58	23	liquid	---	----
59	89	liquid	---	----
60	97	liquid	---	----
61	53	liquid	yes	180-300
62	32	liquid	yes	EP test

[a]Based upon lowest % of heteroatom found by elemental analyses.
[b]Only samples containing epithio group are susceptible to polymerization.
[c]Refers to days of shelf storage.

Four-Ball Wear Tester according to a modified ASTM D 2266-67 procedure (9). Each sample was run for 1 hr at 600 rpm at 120 C under a 50 kg load, with and without an additive. The balls were cleaned with naphtha and hexane, and the scar diameters were measured by use of Precision Scientific Co. microscope assembly.

The extreme pressure tests were made by use of a Precision Scientific Four-Ball Extreme Pressure Tester according to ASTM procedure D 2596-67T (10). Each sample was run at 1440 rpm for 1 min without application of external heat or until balls welded, whichever occurred first. The balls then were washed with solvent, and the scar diameters measured by use of a Precision Scientific microscope assembly.

The weld point loads were reproducible to within ±10 kg.

RESULTS AND DISCUSSION

The performances of the 44 esters, 15 ester-amides and amides, and 2 blended compositions as lubricants and additives for Topaz S105 paraffin oil (T-105) and di-2-ethylhexyl sebacate (DOS) are reported in Table I. The estimated purity of the samples are given in Table II.

Table I shows wear scar values of < 0.5 mm for 10 esters and 4 amides in T-105, and for 13 esters and 4 amides in

DOS. Wear scars of less than 0.6 mm were shown by 20 esters and 7 amides in T-105, and by 27 esters and 6 amides in DOS. In T-105, the most effective antiwear additive among the esters was sample 2, 0.410 mm, and among the amides, sample 57, 0.414 mm. In DOS, the most effective antiwear additives were sample 28, 0.400 mm, for esters and sample 50, 0.418 mm, for the amides. Three of these additives, samples 28, 50, and 57, were phosphorylated derivatives. Generally, the phosphorylated ester derivatives, samples 26, 27, 28, 29, 45, 50, 56, and 57, were consistently more effective than the other fatty ester derivatives. That phosphorylation improved antiwear performance was deduced from tests with amides (3), and confirmed with fatty acid derivatives in general.

Unfortunately, phosphorylation did not improve materially the extreme pressure lubricant performances of the compositions. Its effect was rather innocuous, and rarely beneficial. Thus, although most of the phosphorylated compounds imparted to base oils antiwear characteristics comparable to those of a commercial lubricant, such as Gulfpride Single G, multiviscosity oil, none imparted extreme pressure characteristics similar to those of SAE #90 commercial hypoid fluid.

In extreme pressure lubrication, the epithio compounds were the most consistently effective. As with the amides, the thiirane group -C_SC- invariably enhanced EP performance (weld load) of the neat esters and adversely affected their antiwear performances (3). Most important, however, its presence in the esters made them beneficial antiwear and EP additives for paraffin or diester base oils, sometimes for both, e.g., samples 8, 15, 16, 18, and 21 (Table I). The epithioesters were better than the epithio-amides as additives, with respect to number of beneficial esters and degree of benefit. Thus, for example, 5% of sample 18 or 20 incorporated in one or the other of the base oils produced a lubricant superior to hypoid fluid SAE #90 in EP performance. The epithio derivatives also could function quite regularly as antiwear additives for one or the other base lubricants, and in some instances for both. For example, samples 8, 15, 16, 18, and 21 functioned effectively as both an EP and antiwear additive in both base lubricants.

The sulfurized compounds, samples 22 and 23 (Table I) and some of the pentachlorostearic acid derivatives, samples 40 and 44, also performed well as extreme pressure additives. The bis[2-(pentachlorostearoyloxy)ethyl]sulfone gave the highest EP at weld of any additive at the 5% level in T-105 base oil, but was ineffectual as an antiwear additive and corrosive to the test balls.

The attractiveness of the thiirane group for promotion of desirable lubricant properties is diminished somewhat because it tends to introduce a susceptibility of the compound to polymerize. We noticed that several compounds listed in our last publication (3), as well as several in the present report, tended to polymerize spontaneously upon extended shelf storage. Others, apparently stable during shelf storage, polymerized rapidly at elevated temperatures, 325 C, in the presence of a heavy metal such as lead. For some, the heat generated during the 4-ball EP test was sufficient to initiate polymerization.

The physical state of these polymers ranged from clear gels to clear, rigid, resinlike solids, infusible and practically insoluble in the paraffin and diester base lubricants or conventional solvents. In contrast to their monomeric precursors, they had no capabilities as base lubricants nor, in view of their limited solubilities, as additives for paraffin or diester base oils. However, the polymers were quite soluble in their own and other epithio monomers. The effectiveness of the polymers as lubricant additives in these monomers is presently unknown, and the effects of such polymer-monomer solutions on the antiwear and EP performances of paraffin and diester base oils are also unknown.

Although the polymerization susceptibilities of the ultrapure compounds were not examined, evidence available from the preparative samples showed that polymerization tendency was independent of class of compound. Thus, amides, esters, ester-amides, and heterocyclics, such as the substituted imidazolidines, apparently were equally vulnerable. However, polymerization susceptibility appeared to depend upon the number and spatial relation of the thiirane groups in the compound. Generally, a compound was particularly susceptible if two or more of its moieties each contained a thiirane group. Examples of such compounds are N-methyl-N[2-(9,10-epithiostearoyloxy)ethyl] 9,10-epithiostearamide, 2,3-epithiopropyl 9,10-epithiostearate, and 1,3-bis(9,10,12,13-diepithiostearoyl)imidazolidine. An exception to this generalization was N,N′-bis-(9,10-epithiostearoyl)polyoxypropylenediamine. which showed no tendency to polymerize or gel under storage or accelerated conditions. Compounds containing two closely positioned thiirane groups in the same moiety, e.g., 9,10,12,13-diepithiostearoylmorpholine and 2-ethoxyethyl 9,10,12,13-diepithiostearate, did not polymerize either, nor did compounds containing one thiirane group. Dimerization may not be ruled out, but the presence of dimer was not indicated by anomalies in the bench test evaluations of these materials as lubricants or additives.

The problem of how to effectively stabilize these thiirane compounds remains unsolved. McFadden, et al., (11) claimed that the incorporation of minor amounts of certain thioamides inhibited polymer formation by labile thiiranes which were exposed to bright light and temperature as high as 60 C for longer than 3 weeks. We do not know yet whether such inhibitors will be effective with out compounds. However, the low mol wt thiiranes investigated by the above authors would be considered more reactive than our thiiranes. On the other hand, none of their compounds contained more than one thiirane group, as opposed to two or more in many of ours. The stabilizers of McFadden, et al., (11) might be expected to be very effective with our monothiiranes, and moderately so with compounds which contain more than one thiirane group and which require energetic conditions for polymerization.

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