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Synthesis, Characterization, and Ester-Ester Interchange Study of the Mixed Ester 2-Ethylhexyl Benzyl Azelate

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Chemistry Division

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New components are in demand for low-temperature instrument oils. To meet this demand two new esters, bis(3,4-dichlorobenzyl) β-methyladipate and 2-ethylhexyl benzyl azelate, were synthesized and although both esters possessed the required high surface tensions (43.6 and 33.4 dynes/cm at 20°C, respectively), only the azelate had a suitable viscosity for low-temperature application. This mixed ester, 2-ethylhexyl benzyl azelate, had been prepared by the esterification of the half ester, 2-ethylhexyl hydrogen azelate, with a large excess of benzyl alcohol.

A study was made of the disproportionation of 2-ethylhexyl benzyl azelate into two symmetrical diesters

$$2(\text{2-ethylhexyl benzyl azelate}) \rightleftarrows \text{dibenzyl azelate} + \text{bis(2-ethylhexyl) azelate.}$$

The reaction rates for this ester-ester interchange were found to be too small to restrict the desired application of the mixed ester at temperatures below 100°C.

INTRODUCTION

Background

Stable nonspreading oils for use at temperatures below -40°F are needed to meet present demands for military aircraft and satellite instruments. Recent studies have shown that most oils can be made nonspreading by suitable additives, but that the surface tension of the finished oil should exceed 32 dynes/cm to maintain nonspreading on contaminated surfaces (1). If additives are not used two terminal aromatic groups are usually required to obtain this high a surface tension, but such oils have prohibitively high viscosities at -65°F (2). Blends of aromatic esters with relatively volatile aliphatic esters, such as that of benzylphenylundecanoate with diethylene glycol dicaproate (Specification MIL-L-3918) are useful to -40°F, but no acceptable blend has been found useful at -65°F (3,4). Blends have the further disadvantage that the aliphatic component is somewhat concentrated in the air/oil interface and lowers the surface tension more than might have been anticipated from a uniform mixing of the species.

NRL Problem C02-04; Project RRMA-03-021/652/R001-07-01. This is an interim report; work on the problem is continuing. Manuscript submitted July 14, 1964.

PRELIMINARY STUDIES

In attempting to find components for stable nonspreading low-temperature instrument oils, two new esters, bis(3,4-dichlorobenzyl) β-methyladipate and 2-ethylhexyl benzyl azelate, were synthesized and subjected to various tests to determine if they had the required nonspreading oil properties.

Chlorination of the benzene ring raises the surface tension; therefore the synthesis of bis(3,4-dichlorobenzyl) β-methyladipate (see Appendix) was undertaken by conventional procedures to assess the influence of four such chlorine substituents on the surface tension and viscosity. Effects can be assessed by comparing properties of the chlorinated diester (surface tension 43.6 dynes/cm, viscosity 83.4 centistokes at 100°F (Table 1)) with those of the related unchlorinated diester bis(2-phenylethyl) β-methyladipate (surface tension 41.3 dynes/cm, viscosity 25.07 centistokes at 100°F (Ref. 2)). The small gain in surface tension and the large increase in viscosity resulting from the chlorine substituents demonstrate that chlorination of aromatic esters is not a promising approach to the design in low-temperature nonspreading oils.

The synthesis of 2-ethylhexyl benzyl azelate produced a mixed ester whose properties were suitable for low-temperature nonspreading oil

applications. The synthesis, characterization, and the study of the susceptibility of the mixed ester to disproportionate into the corresponding symmetrical diesters by ester-ester interchange are given in this report.

EXPERIMENTAL

Starting Materials

All of the starting materials are commercial products further purified by conventional methods if required. Azelaic acid, mp 105°-107°C, from Distillation Products Industries was used without further purification. Benzyl alcohol from Fisher Scientific Company was purified by fractional distillation; bp 98°C/10 mm; n_D^{20} 1.5395. Also purified by fractional distillation was 2-ethylhexanol from Distillation Products Industries; bp 75°C/8.0 mm; n_D^{20} 1.4306.

Synthesis of 2-Ethylhexyl Benzyl Azelate

2-Ethylhexyl hydrogen azelate—This compound is prepared by the same procedure that was developed in this Laboratory for the synthesis of 2-ethylhexyl hydrogen sebecate (5). A mixture of azelaic acid (1645 g, 8.74 moles), 2- ethylhexanol (568 g, 4.37 moles), p-toluene sulfonic acid monohydrate (3 g), and 3.5 pints of toluene is refluxed for 2-1/2 hours until 78.5 ml of water is collected in the water trap. After the mixture cools, most of the unreacted azelaic acid is removed by filtration and washed with petroleum ether. The solvents are removed and the esters dissolved in 2.5 pints of petroleum ether and cooled to -5°C. More azelaic acid crystallizes from solution and is filtered out. The solvent is again removed and the mixture is redissolved in 7 pounds of diethyl ether. By washing the ether solution with two 25-ml portions of aqueous 2-percent potassium hydroxide, most of the acid catalyst is removed. By further extraction of the ether layer with aqueous potassium hydroxide and regeneration of the extracted half ester with hydrochloric acid the half ester can be separated from the accompanying azelaic acid and bis(2-ethylhexyl) azelate. During the extractions, the aqueous 2-percent potassium hydroxide is added dropwise beneath the surface to avoid emulsification. Addition of base is continued until the pH of the effluent reaches 10. Most of the diester now remains in the ether layer, which is discarded. A partial acidification with concentrated hydrochloric acid to a pH of 5.5 regenerates the half ester as an oil while azelaic acid remains in solution as potassium salts.

After four such extractions and regenerations the final ether solution is strongly acidified with hydrochloric acid, washed with water, and dried over anhydrous magnesium sulfate. Centrifugal molecular distillation at 75°C and 1 micron furnishes 782 g of product with properties shown in Table 1. Saponification equivalent calculated: 300.4. Found: 299.5.

2-Ethylhexyl benzyl azelate—A mixture of 2-ethylhexyl hydrogen azelate (731.3 g, 2.34 moles), benzyl alcohol (1315 g, 12.17 moles), p-toluene sulfonic acid monohydrate (2 g), and 4 pints of toluene is refluxed for 2 hours until 43.0 ml of water is collected in a water trap.

After the reaction mixture has been neutralized with 0.5-percent aqueous potassium hydroxide washes, solvents are removed by flash evaporation. Then the unreacted benzyl alcohol is removed by molecular distillation at 60°C and 16 microns.

A solution of the residue in 5 liters of heptane is cooled to -80°C. The solid dibenzyl azelate is removed by filtration. The filtrate is recooled and refiltered to remove any further solid. Solvents are removed and the residue is distilled on the centrifugal molecular still at 85° to 100°C and 10 microns. The first 20 percent of the distillate is discarded in order to obtain a product that will not cloud at low temperatures and the last 30 percent is again cooled in heptane to remove dibenzyl azelate and redistilled. Total amount of product after percolation through Florisil is 470 g (50% yield) with properties shown in Table 1. Analysis calculated for $C_{24}H_{38}O_4$: C, 73.81; H, 9.81. Found: C, 73.99; H, 9.76. Saponification equivalent calculated: 195.2. Found 196.5.

Bis(2-ethylhexyl) azelate and dibenzyl azelate—Each ester is prepared by refluxing a mixture containing one mole of azelaic acid, 2.4 moles of the alcohol, 500 ml of toluene, and 0.5 g of p-toluene sulfonic acid monohydrate until the theoretical amount of water is collected in the water trap. Vacuum distillation and percolation through Florisil give neutral products with the properties listed in Table 1.

TABLE 1
Properties of the Esters Synthesized

Compound	Empirical Formula	Molecular Weight (theory)	Boiling Point (°C)	Melting Point (°C)	d_4^{20}	n_D^{20}	Surface Tension 20°C (dynes/cm)	Viscosity, centistokes			
								210°F	100°F	−40°F	−65°F
Bis(3,4-dichlorobenzyl) β-methyladipate	$C_{21}H_{20}Cl_4O_4$	478.20	123/5μ	−20 (glass)	1.3366	1.5588	43.6		83.4		
2-Ethylhexyl hydrogen azelate	$C_{17}H_{32}O_4$	300.43	85/1 μ	−16	0.9640	1.4519					
Bis(2-ethylhexyl) azelate	$C_{25}H_{48}O_4$	412.63	187/.1 mm		0.9156 0.915^{25}*	1.4498	30.6 31.1 †	3.06‡	11.4‡	1,190‡	6,200‡
Dibenzyl azelate	$C_{23}H_{28}O_4$	368.45	207/.1 mm	+15 +5 § pour point	1.0737 1.0702^{25}§	1.5230 1.5236 §	41.6 42.3 §		15.3 §		
2-Ethylhexyl benzyl azelate	$C_{24}H_{38}O_4$	390.54	90/10μ 197/.1 mm (estimated)		0.9848	1.4817	33.4	3.23	12.29	2,086	16,500
Equimolar mixture of bis(2-ethylhexyl) azelate and dibenzyl azelate	$C_{24}H_{38}O_4$	390.54		−5	0.9839	1.4815	32.6	3.25	12.35		

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Procedure for the Ester-Ester Interchange Study

Five-gram samples are sealed in Pyrex tubes at 0.1 mm after being heated to 150°C and agitated for 15 minutes while under vacuum. The samples are heated in an aluminum block at temperatures monitored throughout the reaction time.

In order to detect possible change in acid content, a small portion of the sample is titrated to a pH of 9 in 95% ethanol with 0.1N aqueous potassium hydroxide.

The main portion of the sample is dissolved in 50 ml of heptane and chilled several hours in a bath of dry ice and acetone. This cold material is quickly filtered under vacuum through a medium grade glass filter. The precipitate of dibenzyl azelate is washed with cold heptane and finally dissolved in acetone and transferred to a separate container. The solvent is removed from both the filtrate and the precipitate by flash evaporation. The process is continued for an extra 15 minutes at 60°C and several millimeters of pressure after all apparent solvent has been removed.

The analyses of the three-component mixtures are based on the assumption that equimolar amounts of the two symmetrical diesters are produced during the disproportionation reaction. Thus the weight of the bis(2-ethylhexyl) azelate is 1.12 times the weight of the dibenzyl azelate, the ratio of their molecular weights.

The percent of mixed ester remaining in the sample after undergoing the period of heating can be calculated from the weights of the precipitated dibenzyl azelate and the weight of the filtrate, or alternately, from a measurement of the refractive index of the filtrate. Both procedures gave accurate results when known mixtures of the three esters were analyzed. In the first method the weights of the precipitate and filtrate are used.

p = weight of the dibenzyl azelate
= weight of the precipitate

e = weight of the bis(2-ethylhexyl) azelate
= 1.12p

m = weight of the mixed ester

f = weight of the filtrate = m + e.

Then,

$$\text{weight of the sample} = m + e + p = f + p$$

$$m = f + p - e - p = f - e = f - 1.12p$$

$$\text{The percent of mixed ester in the sample} = \frac{m(100)}{\text{sample weight}} = \frac{100f - 112p}{f + p}.$$

The second method utilizes the refractive index of the filtrate which contains the mixed ester and the bis(2-ethylhexyl) azelate. In a two-component mixture

$$X(1.4498) + (100 - X)(1.4820) = 100\ n_D^{20} \text{ of the filtrate}$$

$$X = \frac{148.20 - 100\ n_D^{20} \text{ of the filtrate}}{0.0322}$$

where X = volume percent of bis(2-ethylhexyl) azelate, n_D^{20} 1.4498.

(100 - X) = volume percent of the mixed ester, n_D^{20} 1.4820, in the filtrate.

For the original three-component sample,

$$\text{the percent volume of mixed ester in the sample} = \frac{(100 - X)100}{X + (100 - X) + (0.76X)} = \frac{(100 - X)100}{100 + 0.76X}$$

(0.76X) = the relative volume of dibenzyl azelate formed, where (0.76) is the ratio of the equimolar volume of dibenzyl azelate to that of bis(2-ethylhexyl) azelate.

Because of the similarity of the interchange products to the mixed ester, the relative amounts of mixed ester expressed as percent by weight, percent by volume, and mole percent are essentially the same.

CHARACTERIZATION OF 2-ETHYLHEXYL BENZYL AZELATE

Problem of Synthesis

For this study the mixed ester, 2-ethylhexyl benzyl azelate (ABE), is required in high purity. Usual esterification methods result in the concurrent production of the two symmetrical diesters, bis(2-ethylhexyl) azelate (AEE) and dibenzyl azelate (ABB). Separation of the mixed ester from the three-component mixture by distillation is difficult and inefficient since the boiling points of all three compounds lie between 187°C and 207°C at 0.1 mm. Such a separation is further complicated by the possibility of ester-ester interchange, or disproportionation of the mixed ester to the unwanted symmetrical compounds at the temperature of distillation. Experiment showed that the dibenzyl azelate is readily precipitated by chilling a heptane solution of the three compounds. It was therefore desirable to choose conditions for the synthesis that would minimize the production of bis(2-ethylhexyl) azelate.

One method of synthesis is to esterify 2-ethylhexyl hydrogen azelate (AHE) with benzyl alcohol (BOH),

$$\text{AHE} + \text{BOH} \rightarrow \text{ABE} + H_2O \uparrow \cdot \qquad (1)$$

Other significant reactions might include the alcoholysis of the resulting mixed ester with more benzyl alcohol to form dibenzyl azelate and 2-ethylhexanol (EOH)

$$\text{ABE} + \text{BOH} \rightleftharpoons \text{ABB} + \text{EOH} \cdot \qquad (2)$$

Any resulting 2-ethylhexanol from Eq. (2) could form unwanted bis(2-ethylhexyl) azelate either by alcoholysis of the mixed ester

$$\text{ABE} + \text{EOH} \rightleftharpoons \text{AEE} + \text{BOH}, \qquad (3)$$

or by direct esterification of the half ester

$$\text{AHE} + \text{EOH} \rightarrow \text{AEE} + H_2O \uparrow \cdot \qquad (4)$$

An esterification of a stoichiometric mixture of the half ester and benzyl alcohol resulted in the production of the mixed ester and approximately 10 percent of each symmetrical diester. Thus the products of alcoholysis are significantly large during the reaction.

The use of excess benzyl alcohol for the esterification should decrease the amount of bis(2-ethylhexyl) azelate formed in Eqs. (3) and (4). A severalfold excess of benzyl alcohol substantially increases the rates of Eqs. (1) and (2) and decreases

the rates of Eqs. (3) and (4) by dilution of the reactants. Since esterification with excess alcohol can be carried out almost to completion in a much shorter time than with stoichiometric amounts of reactants, the unwanted side reactions of Eqs. (3) and (4) are allowed a much shorter time to run.

In the actual synthesis, five times the stoichiometric amount of benzyl alcohol is reacted with the 2-ethylhexyl hydrogen azelate. To minimize alcoholysis of the product, the reaction is terminated when approximately 98 percent of the theoretical amount of water of esterification is collected.

Determination of Purity

Many properties of the synthesized mixed ester are found to be essentially the same as those of an equimolar mixture of the two symmetrical diesters. These properties include density, refractive index (Table 1), saponification equivalent, and elemental analyses. (Experimental section.) Therefore, measurement of these properties alone gives little indication of the purity of the product because a mixed ester sample containing an equimolar mixture of the two symmetrical diesters in any amount would also have these similar characteristics. However, it can be shown that the actual amounts of the symmetrical diesters present must be low.

Practically all of the dibenzyl azelate was removed from the product by precipitation in cold heptane. Quantitative experiments with mixtures of dibenzyl azelate and bis(2-ethylhexyl) azelate indicate that this technique leaves less than 0.5 percent residual dibenzyl azelate. The maximum amount of dibenzyl azelate in the product is accordingly estimated at less than one percent. Since this mixed ester sample also has the properties of an equimolar mixture of the two symmetrical diesters, it can now be inferred that the molar amount of bis(2-ethylhexyl) azelate present is similar to the amount of the dibenzyl azelate, or less than one percent.

Another way to infer the purity of the mixed ester is by the estimation of relative amounts of benzyl groups in ester samples as indicated by the absorbancy of the infrared band at 14.35μ. Theoretically, the equimolar mixture and the mixed ester have the same relative amounts of benzyl groups. A three-component mixture of the two symmetrical diesters and the mixed ester will contain a similar amount of benzyl groups only if equimolar amounts of the two symmetrical diesters are present. The absorbancy band at 14.35μ is actually slightly stronger for the mixed ester sample than for the equimolar mixture. This is interpreted to mean that in the mixed ester sample, which also contains some amount of the other two diesters, the dibenzyl azelate is present in a larger amount than the bis(2-ethylhexyl) azelate. Since the presence of dibenzyl azelate was previously shown to be less than one percent in the mixed ester sample, an even smaller amount of bis(2-ethylhexyl) azelate must be present. Therefore, all the evidence points to a mixed ester sample containing less than one percent each of dibenzyl azelate and bis(2-ethylhexyl) azelate.

Significant Properties

All surface tensions were determined by the ring method and are shown in Table 1. A value of 33.4 was observed for the mixed ester. For reasons mentioned previously, a lower value for the surface tension of the equimolar mixture of the two symmetrical diesters would be expected. In this case, 32.6 was found.

It is seen in Table 1 that the viscosities for the mixed ester and for an equimolar mixture of the two diesters are about the same at 210°F and 100°F. However, the equimolar mixture freezes in the vicinity of 25°F while the mixed ester remains liquid at very low temperatures. This is one striking difference between the two materials.

A study of behavior during low-temperature storage was made with samples sealed in Pyrex tubes at 0.1 mm after being heated to 320°F and shaken for 15 minutes under vacuum. Samples of early fractions in the distillation of the mixed ester clouded at -40°F. This slight clouding is the reason for discarding the initial 20 percent of the distillate as stated before. Absolutely no clouding or freezing is observed in mixed ester samples stored a week at -40°F, -65°F, and -100°F. The addition of bis(2-ethylhexyl) azelate produces no clouding except for the small amount observed in both commercial and NRL-prepared diester samples. Neither clouding nor freezing is observed under the same conditions in samples containing 5 and 7 percent of dibenzyl azelate.

However, a sample containing 10 percent of dibenzyl azelate clouds at -10°F and becomes solid at -20°F.

ESTER-ESTER INTERCHANGE STUDY OF 2-ETHYLHEXYL BENZYL AZELATE

It is known that a mixture of two symmetrical diesters of a dibasic acid, under the influence of temperature and catalysts, undergoes an ester-ester interchange reaction which involves a redistribution of the two acyl radicals. At equilibrium, a purely statistical distribution of the components exists which is not influenced by temperatures changes (6).

Therefore, 2-ethylhexyl benzyl azelate is expected to disproportionate until an equilibrium mixture exists which is composed of 50 mole percent mixed ester, 25 mole percent of dibenzyl azelate, and 25 mole percent of bis(2-ethylhexyl) azelate. This is represented by the following equation:

$$2\ \text{ABE} \rightleftarrows \text{ABB} + \text{AEE} \cdot \qquad (5)$$

Many of the properties of the mixed ester are not appreciably altered by the ester-ester interchange. However, if sufficient dibenzyl azelate is formed, the material becomes unsuitable for use as a low-temperature lubricant. It was therefore necessary to determine if the interchange would be rapid enough to restrict the useful life of the oil.

To study this reaction, samples of mixed ester were maintained at desired temperatures for definite times and then analyzed by methods described in the Experimental Section.

The experimental data from the study of the interchange reaction are tabulated in Table 2. To observe the effect on the rate of the reaction, several runs were made with an added 0.5 percent of azelaic acid. Apparent rate constants, k's, are calculated according to the kinetics of a second-order reversible reaction with a statistical equilibrium constant. Data from the study of the acidolysis reaction of 2-ethylhexyl hydrogen sebacate (5), which has some points of similarity

TABLE 2
Experimental Data and Rates for Ester-Ester Interchange of 2-Ethylhexyl Benzyl Azelate

Run	°C	Time (days)	Catalyst Added	Meq Acid Per Gram of Sample		Mixed Ester Reacted (percent)	k $\left(\frac{10^4}{\%\ \text{Days}}\right)$
				Initial	Final		
	202	(0)	(None)	(0.0006)	(0.0006)		0.13*
1	202	18	None	0.0006	0.0014	2.6	0.15
2	202	24	None	0.0006	0.0015	2.8	0.12
3	202	24	0.5% azelaic acid	0.050	0.052	11.5	0.54
	233	(0)	(None)	(0.0006)	(0.0006)		0.55†
4	233	2.85	None	0.0006	0.010	1.7	0.61
5	233	14	None	0.0006	0.052	13.0	1.1
6	233	33.9	None	0.0006	0.163	41.2	2.6
	246	(0)	(None)	(0.0006)	(0.0006)		1.0†
7	246	1.95	None	0.0006	0.018	2.4	1.3
8	246	4.25	None	0.0006	0.036	5.4	1.3
9	246	6.25	None	0.0006	0.048	8.9	1.6
10	246	0.75	0.5% azelaic acid	0.048	0.055	3.5	4.8
11	246	1	0.5% azelaic acid	0.048	0.062	4.8	5.0

* The mean value is used since no rise in k was found experimentally.
† Found by extrapolation to zero time.

to this study, were found to fit this scheme and it was considered also to apply to the mixed ester interchange reaction. For this type of reaction

$$k = \frac{2.303}{2\ C_0 t} \log \left[\frac{0.5C_0}{0.5C_0 - (C_0 - C)} \right]$$

where C_0 is the initial concentration, 100 percent, and C is the concentration after time t (7).

Calculated rate constants are observed to vary at a given temperature. A considerable upward drift of k occurs with increasing time in runs 4-6. It is also noted that the final acid content increases with time. When 0.5 percent of azelaic acid is added, the calculated rate constant increases substantially. All this demonstrates that the rate of ester-ester interchange is catalyzed by the acid. This increase of acid content during a run is caused by the pyrolysis of the ester (8), which occurs to some extent along with the interchange.

Table 3 shows the acidity produced by pyrolysis of the mixed ester and each of the diesters at 246°C for 6.25 days. That the extent of pyrolysis would be greater for bis(2-ethylhexyl) azelate than for dibenzyl azelate at this temperature is suggested by several other studies (8,9). Extent of pyrolysis, as evidenced by acid formed, is experimentally found to lie between that of the two diesters.

The catalytic effect of the acid formed by pyrolysis presents a problem when comparing calculated rate constants at different temperatures. By plotting the calculated rate constants versus time for each temperature and extrapolating to zero time, rate constants are obtained for systems in which there has been no acid produced by pyrolysis. These reaction rate constants for zero time, also shown in Table 2, were used to construct the Arrhenius plot shown in Fig. 1. From the slope of the line, the energy of activation is determined to be 23 kcal per mole. A similar plot, not shown, for the rate constants of the systems containing 0.5 percent of azelaic acid produced a not-quite parallel line about 0.7 of a logarithmic unit above the previous one, indicating a value of 25 kcal per mole for the energy of activation. Differences in these two values probably reflect experimental error since a catalyst generally lowers the apparent energy of activation.

The rate constants of interchange at other temperatures can be estimated from an extrapolation of the experimentally constructed line as shown in Fig. 1. For example, the rate constant for interchange at 100°C is 1.8×10^{-8}/(percent)(days). This would mean that at 100°C, 15 years would be required for 1 percent of the mixed ester to react. Table 4 lists the time required for 1 percent of the mixed ester to undergo interchange at a number of temperatures. No attempt is made to allow for the catalytic effect of the acid produced by the concurrent pyrolysis. This 1-percent interchange is not a critical limitation to practical use of the oil. In fact, substantially more interchange could occur without decreasing the value of the material as a component for a low-temperature instrument oil.

Figure 1 also shows a similarly constructed plot for the pyrolysis of the mixed ester. First-order rate constants, obtained from the amount of acid generated during the runs, are based on the assumption that an acid group is produced for each molecule of ester pyrolyzed during the early stages of the reaction. In order that the initial rates for interchange and pyrolysis will

TABLE 3
Results of Pyrolysis of the Mixed Ester and Diesters at 246°C for 6.25 Days

Compound	Meq of Acid Per Gram of Sample	Pyrolyzed* (percent)
Bis(2-ethylhexyl) azelate	.0692	2.7
2-Ethylhexyl benzyl azelate	.0510	2.0
Dibenzyl azelate	.0354	1.4

*Calculated on the assumption that one acid group is produced for each molecule of ester pyrolyzed.

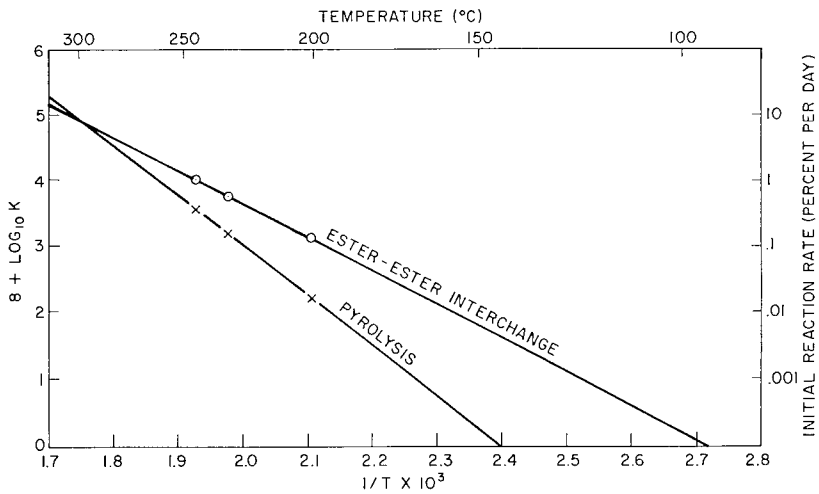

Fig. 1 - Temperature dependence of initial reaction rates of ester-ester interchange and pyrolysis of 2-ethylhexyl benzyl azelate

TABLE 4
Time Required for 1 Percent of the Mixed Ester to Undergo Interchange at Various Temperatures

Temp (°C)	Time
100	15 years
150	110 days
202	8 days
233	2 days
246	1 day
290	4 hours

have the same meaning, the actual pyrolysis rate constants must be divided by 100 before they are plotted. The slope of the plot for pyrolysis indicates an energy of activation of 36 kcal per mole. At about 290°C the two lines intersect, indicating identical initial rates for the two reactions. As the temperature decreases the pyrolysis reaction becomes much slower than the ester-ester interchange. Below 200°C, pyrolytic production of acid catalyst becomes too small to affect the rate of ester-ester interchange. At 100°C, the rate of pyrolysis is only about 1/1000 that of interchange.

CONCLUSIONS AND RECOMMENDATIONS

The mixed ester, 2-ethylhexyl benzyl azelate, has a surface tension of 33.4 dynes per cm at 20°C, no observed clouding or freezing at −100°F, and a viscosity of 16,500 centistokes at −65°F; these properties make it a promising component for a nonspreading low-temperature oil.

Reaction rates were studied for the ester-ester interchange reaction, 2[2-ethylhexyl benzyl azelate] ⇄dibenzyl azelate + bis(2-ethylhexyl) azelate. Disproportionation at 100°C, the highest temperature to which the oil would be normally subjected, would not restrict the desired application since it is estimated that only one percent would react in 15 years.

It is recommended that further studies be made of the mixed ester, 2-ethylhexyl benzyl azelate, for the formulation of a practical low-temperature nonspreading instrument oil.

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Appendix

SYNTHESIS OF BIS(3,4-DICHLOROBENZYL) β-METHYL ADIPATE

STARTING MATERIALS

All starting materials were commercial products further purified by conventional methods if required. The 3,4-dichlorobenzoic acid (mp 201°-202°C) from Distillation Products Industries was used without further purification. The β-methyladipic acid (mp 96°-98°C) from Columbia Organic Chemicals was recrystallized from water. Neutralization equivalent calculated: 80.08. Found: 79.92.

SYNTHESIS

Butyl 3,4-dichlorobenzoate

This ester is required as an intermediate for preparing 3,4-dichlorobenzyl alcohol. A mixture of 3,4-dichlorobenzoic acid (382.0 g, 2.11 moles), 1-butanol (185.3 g, 2.50 moles), toluene (1000 ml), and p-toluenesulfonic acid monohydrate (1.0 g) is refluxed for 40 hours. Water collected in the Dean and Stark water trap amounts to 36.9 ml (theory 36.02 ml). After diluting the reaction mixture with ether (1 lb), the ether mixture is washed with 2-percent aqueous potassium carbonate, dried over magnesium sulfate and then distilled to afford 494.2 g (85.2% yield) of product; bp 110°C/0.3 mm; n_D^{20} 1.5301; d_4^{20} 1.2291. Saponification equivalent calculated: 247.1. Found: 239.0.

3,4-Dicholorobenzyl alcohol

This alcohol is prepared by a modification of the ester reduction procedure of Nystrom and Brown (A1). Butyl 3,4-dichlorobenzoate (420.1 g, 1.70 moles) is added over a 3-hour period to a stirred mixture of pulverized lithium aluminum hydride (41.7 g, 1.10 moles) and dry ether (1920 ml). With continued stirring, strong external cooling is applied to the flask to reduce the temperature of its contents to about 0°C. These conditions are maintained during the cautious addition of water (220 ml) and the subsequent addition of 20-percent aqueous sodium hydroxide solution (67.2 g, 0.336 mole). The resulting ether layer and ether extracts (2 × 300 ml) are combined and distilled to furnish 392.0 g (94.0% yield) of product; bp 110°C/0.3 mm; mp 38.5°-39.5°C (mp 38°C in Ref. A2).

Bis(3,4-dichlorobenzyl) β-methyladipate

A mixture of 3,4-dichlorobenzyl alcohol (276.2 g, 1.56 moles), β-methyladipic acid (116.9 g, 1.56 moles), p-toluenesulfonic acid monohydrate (1.5 g), and toluene (300 ml) is refluxed for 8 hours. The theoretical amount of water (26.3 ml) is collected in the water trap. After the usual workup of the reaction mixture, molecular distillation yields 282.5 g (80.8% yield) of product with the properties shown in Table 1. Analysis calculated for $C_{21}H_{20}Cl_4O_4$: C, 52.74; H, 4.22; Cl, 29.66. Found: C, 52.85; H, 4.52; Cl, 29.14. Saponification equivalent calculated: 115.20. Found: 115.5.

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New components are in demand for low-temperature instrument oils. To meet this demand two new esters, bis(3,4-dichlorobenzyl)β-methyladipate and 2-ethylhexyl benzyl azelate, were synthesized and although both esters possessed the required high surface tensions (43.6 and 33.4 dynes/cm at 20°C, respectively), only the azelate had a suitable viscosity for low-temperature application. This mixed ester, 2-ethylhexyl benzyl azelate, had been prepared by the esterification of the half ester, 2-ethylhexyl hydrogen azelate, with a large excess of benzyl alcohol.

A study was made of the disproportionation of 2-ethylhexyl benzyl azelate into two symmetrical diesters

$$2(\text{2-ethylhexyl benzyl azelate}) \begin{matrix} \rightarrow \text{dibenzyl} \\ \leftarrow \text{azelate} \end{matrix} + \begin{matrix} \text{bis(2-ethylhexyl)} \\ \text{azelate} \end{matrix} .$$

The reaction rates for this ester-ester interchange were found to be too small to restrict the desired application of the mixed ester at temperatures below 100°C.

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