of dehydrodehalogenation with potassium hydroxide was made more feasible for analytical, as well as preparatory, work by employing ethylene glycol as the solvent rather than the ordinary alcohols simplifying isolation and purification of the stearolic acid.

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Hydrazine-Reduced Linolenic Acids as a Source of C_9, C_{12}, and C_{15} Dibasic Acids[1]

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Abstract

Anticipated reduction in cost of hydrazine, resulting from its increased production as a rocket fuel, suggests the need to reconsider this chemical as an industrial reactant for fats. Hydrazine reduces the individual double bonds of linolenic acid (9,12,15-octadecatrienoic acid) nonselectively and without altering the position of residual unsaturation; thus the monoene fraction from hydrazine-reduced linolenic acid consists of an equimixture of the 9-, 12-, and 15-octadecenoate acids. Equal amounts of the C_9, C_{12}, and C_{15} dibasic acids are derived from this fatty acid mixture by oxidative cleavage along with the corresponding monobasic acids.

Kinetics of reactions, source of raw materials and reactants, and problems of processing and utilization of products are discussed.

Introduction

LINOLENIC ACID by virtue of unsaturation at the 9, 12, and 15 carbon atoms constitutes a potentially unique commercial source of C_{15} dibasic acid. Required processing steps are reduction to the monoene level and oxidative cleavage at the double bond.

Recent studies have demonstrated not only that catalytically hydrogenated methyl linolenate is a complex mixture composed of saturates, monoenes, dienes, and trienes but that these classes of compounds are composed of numerous *cis* and *trans* isomers and positional isomers (1). Within the monoene fraction alone, nine components were demonstrated by capillary gas chromatography. Dibasic acid analysis indicated that the original double bonds at positions 9, 12, and 15 had moved to neighboring carbon atoms in nearly a random fashion. The dibasic acids, resulting from such a complex system, present a mixture difficult to fractionate by current processing equipment. Although catalytic hydrogenation of alkali-conjugated linoleic acid soaps (2) produces a mixture of 9, 10, 11, and 12 monoenes, it cannot yield the C_{15} dibasic acid available from linolenic acid.

In contrast with the complex mixture of isomeric monoenes obtained by the heterogeneous catalytic reduction of methyl linolenate, the monoenes from the homogeneous reduction with hydrazine are composed of 9-, 12-, and 15-octadecenoic acids exclusively. They are present in approximately equal amounts (3) and, as Aylward and Rao (4) demonstrated earlier, have no isomers. The monoenes from hydrazine-reduced linolenic acids might thus be expected to produce an approximately equal mixture of the saturated C_9, C_{12}, and C_{15} dibasic acids upon oxidative cleavage.

Anticipated reduction in cost of hydrazine, resulting from its production for a rocket fuel, suggests the need for reconsideration of this chemical as an industrial reactant for fats (5). By 1951 the price for hydrazine hydrate had dropped from a previous high of \$5 per pound to \$3.50 per pound. Currently it sells for \$1.28. Estimates indicate that hydrazine produced by neutron irradiation of ammonia may result in prices as low as 15 to 25 cents per pound, depending upon rate of production. At this price, the chemical cost for reluction of a double bond per pound of linolenic acid is about 2½ cents. Depending upon yields, efficiency of the reaction, and value of the products, hydrazine reduction may become an economically feasible reaction. The present paper reviews the kinetic information on the reaction, considers certain schemes for processing, and presents certain experimental verifications of these concepts.

Mechanism of Hydrazine Reduction. A startling observation was made by Aylward that oxygen must be present if hydrazine reduction was to take place (4). This phenomenon was early verified in our experiments, but the complete mechanism was not known. Our experiments indicated that, based upon measurements of oxygen taken up, of nitrogen evolved, and of hydrazine reduced, the absorption of one-half mole of oxygen resulted in the liberation of

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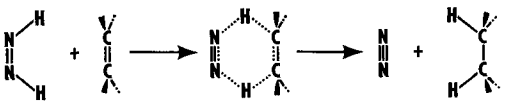
TABLE I

Scheme of Approximate Yields for Fatty Acid Isomers and Derived Dibasic Acids

Yield of dibasic acids		Fatty acids	Yield of isomeric fatty-acids
1 C_9	O_3 ←	9,12,15-Octadecatrienoic	....
⅔ C_9	O_3 ←	9,12-Octadecadienoic	⅓
		9,15-Octadecadienoic	⅓
⅓ C_{12}		12,15-Octadecadienoic	⅓
⅓ C_9	O_3 ←	9-Octadecenoic	⅓
⅓ C_{12}		12-Octadecenoic	⅓
⅓ C_{15}		15-Octadecenoic	⅓
		Octadecanoic	....

one mole of nitrogen and the reduction of one double bond. Aylward, however, suggests that 2 moles of hydrazine and 3/2 mole of oxygen are required to reduce one double bond (6). Aylward, who also found that the presence of a weak acid was necessary, suggests that the hydrazonium ion is the effective reducing agent (7).

Corey, Mock, and Pasto (8) and Hünig, Müller, and Thier (9) recently proposed mechanisms with the diimide intermediate as follows:



The diimide is formed by partial oxidation of hydrazine and explains why oxygen is required to achieve reduction.

Kinetics. Evidence for nonselective reduction of unsaturation at the 9, 12, and 15 positions in linolenic acid has been published (3). Countercurrent distribution was used to separate the saturates, monoenes, dienes, and trienes; capillary gas chromatography and dibasic acid analysis served to identify the position of double bonds and the amount of isomers produced. Infrared spectrometry demonstrated the absence of *trans* isomers. The sequences of steps and intermediates are summarized in Table I. There is definite evidence that the bonds closest to the alkyl end of the molecule are reduced slightly more rapidly than those nearer the carboxyl of the molecule; however, for purposes of discussion, it is assumed the 9, 12, and 15 monoenes are present in approximately one-third amounts. It is apparent from the first column of Table I that the C_{15} dibasic acid can only be derived from the monoene fraction and that the C_{12} dibasic acid can be derived from both the monoene and diene fractions. Since azelaic acid is immediately and commercially available from a variety of fatty acid sources and because C_{15} dibasic acid is unique to linolenic acid reduction, the reaction should be conducted so as to maximize the 15-monoene content and to minimize the stearic acid and those dienoic and monoenoic isomers that yield azelaic acid.

A first-order reaction rate has been observed for the hydrazine reaction (10). Specific reaction rates for triene, diene, and monoene have been determined with the use of C_{14}-labeled linoleic acid and are in the approximate ratio of number of double bonds present; namely, 3.41 to 2 to 1, respectively. The course of the reaction starting with linolenic acid has been calculated from these specific reaction rates (Fig. 1). It is apparent from these curves that the maximum monoene which may be expected is in the range of 40–43%. By proper selection of the degree of reduction within this range, minimum stearic acid may be achieved, but at the expense of obtaining higher diene and triene contents. A near optimal composition has been achieved experimentally as described below, and these data points are included on Figure 1.

Source of Raw Material. Linolenic acid, in a mixture of fatty acids, is available in limited supply as the soap stock from alkali refining of linseed oil. This fatty acid mixture, containing 50–59% linolenic acid, is also available in volume by the hydrolysis of linseed oil. Other fatty acids present in both these raw materials would be approximately 15% linoleic acid, 16% oleic acid, 4% stearic acid, and 7% palmitic acid. Although the crude mixture of fatty acids from soap stock may well serve to be the practical starting material for hydrazine reduction, 95% pure linolenic acid can be produced on pilot-plant scale at a rate of approximately 1 lb per hour using continuous liquid-liquid extraction (11). The scale-up between this pilot-plant operation and commercial operations is of the order of a thousandfold. Experience in azelaic acid production indicates that the purification of starting materials simplifies subsequent isolation of dibasic acids. In this manuscript both pure linoleic and linseed fatty acids are used as raw materials.

Direct Ozonization VERSUS *Fractionation-Recycle-Ozonization.* If it is assumed that the hydrazine reduction has been carried to the optimal point, two approaches to processing and oxidative cleavage present themselves: (a) the reduction mixture could be ozonized direct, and (b) the monoene-saturate could be separated and the diene-triene fraction added back to the starting linolenic acid and reduced again along with a fresh batch of triene before ozonization.

An estimate of the composition of the resultant dibasic acids from these two approaches can be calculated as shown in Table II. Direct ozonization of the stearate results only in its reisolation. The 43.6% of monoene is assumed to give equal parts, 14.5%, of the three dibasic acids; whereas the diene fraction gives

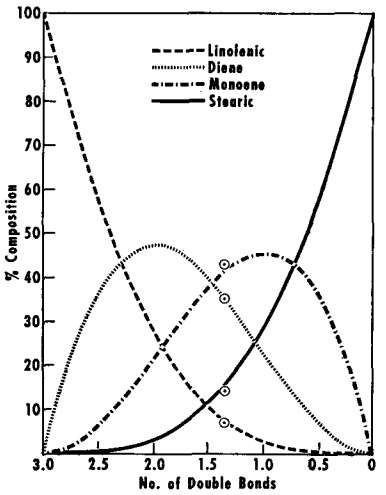


FIG. 1. Kinetics for hydrazine reduction of linolenic acid calculated with ratios $k_{triene}::k_{diene}::k_{monoene}$ of 3.41::2::1, respectively. Circles represent the composition of the laboratory-scale reduction.

twice as much C_9 as C_{12}. The residual linolenic acid yields only azelaic acid. The summary calculation for direct ozonization with these assumptions of 100% yield on oxidative cleavage and of no selectivity with respect to double bonds is 14.0% stearate, 45.2% azelaic, 26.2% dodecanedioic acid, and 14.5% pentadecanedioic acid.

Under the fractionation-recycle-ozonization scheme shown in the lower half of Table II, the monoene-stearate fraction would be ozonized directly but the diene-triene fraction would be recycled back into the hydrazine-reduction step. If the optimal reduction were obtained for the 35.2% diene approximately equal amounts of diene (15.9%) and of monoene (15.9%), with 3.5% stearate would be obtained. The 15.9% of monoene would yield 5.3% each of C_9, C_{12}, and C_{15} dibasic acid. If fractionation-recycle operation shown in Table II were continued until all the 15.9% diene were consumed, the molar percentages of stearic acid and of C_9, C_{12}, and C_{15} dibasic acids would be 21.9, 26.0, 26.0, 26.0, respectively.

The qualitative conclusion apparent from these calculations is that, compared to direct ozonization, the fractionation-recycle procedure increases yield of C_{15} dibasic acid, decreases yield of C_9 dibasic acid, but increases yield of stearic acid. The decision as to whether direct ozonization or the "fractionation-recycle-ozonization" scheme is the more desirable de-

TABLE II

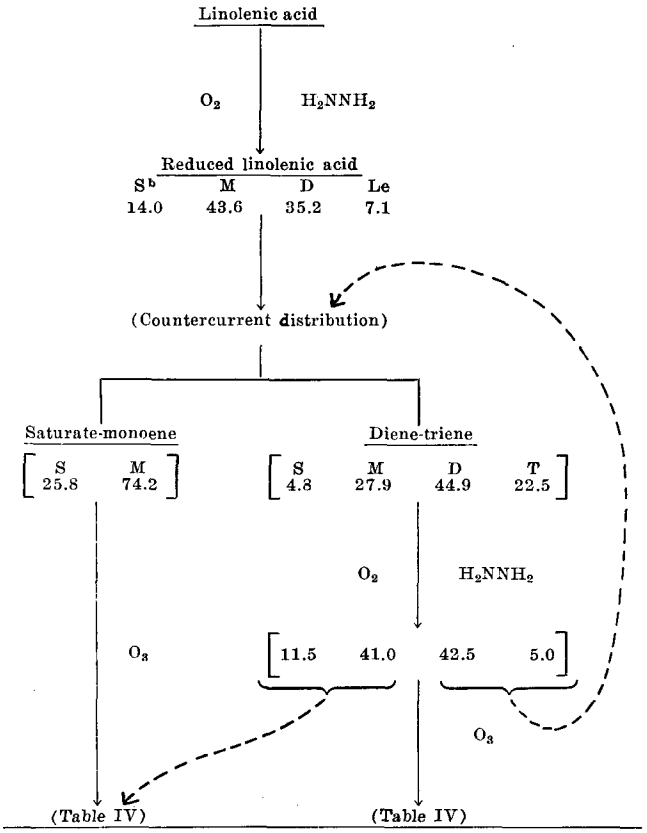
Comparison of Calculated Yields for Direct Ozonization vs. Fractionation-Recycle-Ozonization

				Composition of ozonized acids[a]			
				S	C_9	C_{12}	C_{15}
Direct Ozonization							
Linolenic acid 100							
$\downarrow N_2H_4$							
Le	D	M	S				
7.2	35.2	43.6	14.0				
			O_3 →	14.0	45.2	26.2	14.5
Fractionation-Recycle							
Linolenic acid 100							
$\downarrow N_2H_4$							
Le	D	M	S				
7.2	35.2	43.6	14.0				
			O_3 →	14.0	14.5	14.5	14.5
	N_2H_4						
	D	M	S				
	15.9	15.9	3.5				
			O_3 →	3.5	5.3	5.3	5.3
	N_2H_4						
	D	M	S				
	7.2	7.2	1.6				
			O_3 →	1.6	2.4	2.4	2.4
	N_2H_4						
	D	M	S				
	3.3	3.3	0.7				
			O_3 →	0.7	1.1	1.1	1.1
	N_2H_4						
	D	M	S				
	1.5	1.5	0.3				
			O_3 →	0.3	0.5	0.5	0.5
	N_2H_4						
	D	M	S				
	0.6	0.6	0.1				
			O_3 →	0.1	0.2	0.2	0.2
			Total	20.2	24.0	24.0	24.0
			Normalized[b]	21.7	26.1	26.1	26.1

[a] S = Stearic, M = Monoenoic, D = Dienoic, Le = Linolenic.
[b] Normalized to account for the 7.2% linolenic acid and 0.6% dienoic acid not reduced.

TABLE III

Experimental Reduction, Fractionation, and Recycle[a]



[a] All figures in percentages.
[b] See footnote "a" in Table II for key.

pends on a knowledge of the value of products obtained, in addition to many processing factors. Because one has no way of determining the commercial value of a new product, such as the C_{15} dibasic acid, further speculation as to the relative merits of these two approaches seems unwarranted.

There is some element of practicability for the fractionation scheme outlined in separating the saturate-monoene fraction from the diene-triene fraction. Studies at this laboratory have demonstrated that it is possible to fractionate safflower oil (12) into a high-purity linoleic acid fraction and a residual monoene and saturated fraction. Thus the separation of a monoene-saturate fraction from the diene-triene fraction anticipated here has its prototype in pilot-plant experience.

Laboratory Experimentation. In an attempt to get experimental verification for the concepts described, a sample of linolenic acid produced by liquid-liquid extraction from linseed oil was reduced with hydrazine. The resultant mixture was separated into monoene-saturate and diene-triene fractions by countercurrent distribution. After re-reduction of the diene-triene fraction, both fractions were ozonized and the products analyzed. Details of this reduction are as follows: One hundred grams of linolenic acid (iodine value −247) were heated to 50C with 1 liter of ethyl alcohol and 87 ml of hydrazine hydrate for 5 hr while air was passed through the solution. The degree of the reaction was followed by periodic sampling and analysis by gas-liquid chromatography. The reaction was stopped as previously noted at a near optimal composition of 7.1% triene, 35.2% diene, 43.6% monoene, and 14% stearate (Fig. 1 and Table III). After dilution of the reaction mixture with

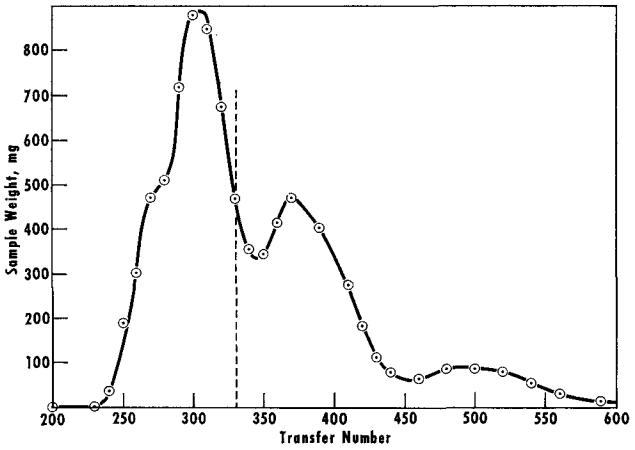


FIG. 2. Preparative countercurrent distribution of laboratory-reduced linolenic acid.

water, the solution was acidified and fatty acids were recovered by extraction with petroleum ether. Methyl esters were formed by esterification with methanol using sulfuric acid catalyst. After distillation, 53 g of esters were fractionated by counter-current distribution between acetonitrile and pentane-hexane. This gross overloading of the countercurrent distribution system resulted in what is considered to be poor resolution for analytical work but satisfactory for preparative separations. A shown in Figure 2, the split between the triene-diene and the monoene-saturate fraction was made so as to give the monoene portion relatively free from diene and triene. The 25 g of the monoene-saturate fraction was then oxidatively cleaved both on an analytical scale with permanganate periodate and on a preparative scale with ozone. In agreement with prior results, the analytical figures show that the major components are the C_9, C_{12}, and C_{15} dibasic acids (Table IV). The diene-triene fraction comprising 22.6 g was saponified to the free acids then re-reduced with hydrazine. The reduction was carried to a nearly optimal point for recycling as indicated by the broken line in Table III. The analytical figures of Table IV for dibasic acids demonstrate the relatively low yields of the desired C_{12} and C_{15} dibasic acids that result on direct ozonization.

Preparative-scale ozonization of the monoene-saturate fraction (20.0 g as the methyl esters) and oxidative decomposition of the ozonolysis products were carried out according to the procedure described by Ackman et al. (13). This procedure, which gives a minimum of chain degradation products, involves ozonization in methanol, evaporation of solvent to isolate the ozonolysis products, and oxidation of the latter with performic acid. The monocarboxylic acids and half-esters after removal of formic acid, were converted to the methyl and dimethyl esters in metha-

TABLE IV
Dibasic Acid Composition of Fractions, %

	Monoene-saturate		Reduced diene-triene
C atom no.	Anal.	Isolation	Anal.
4	....	....	0.2
5	....	0.2	0.2
6	0.2	....	5.0
7	0.3	0.3	0.9
8	1.5	....	3.4
9	36.8	39.2	52.3
10	0.7	0.3	1.4
11	4.5	1.4	1.1
12	35.5	36.5	25.3
13	0.1	0.2	....
14	0.2	0.3	0.3
15	20.3	21.6	10.4
16	....	....	0.3

TABLE V
Dimethyl Esters of Dibasic Acids—Spinning Band Distillation

C atom no.	Wt % of distilland	Purity, %
9	10	92
12	9	87
15	5	90

nol and 2,2-dimethoxypropane in the presence of hydrogen chloride. After washing, drying, and removing the solvent, each product was distilled through a spinning band column under reduced pressure. Analyses by gas chromatography were made on the various fractions. The yield of recovered difunctional cleavage products was 72% and recovery of methyl stearate was 89%. The presence of methyl stearate apparently prevented sharp separation of fractions, but purities on the order of 90% were obtained for the major C_9, C_{12}, and C_{15} dimethyl ester fractions (Table V). Summation of the various fractions gave the over-all composition presented in Table IV under the heading "Isolation." The agreement between the analytical figures and the isolation figures assures us that there were little selective losses of the dibasic acids.

In order to determine if better separation could be effected in the absence of methyl stearate, hydrazine-reduced linseed fatty acid methyl esters from another experiment were fractionally crystallized to remove the saturates. GLC analysis of the methyl esters thus purified indicated the following composition: methyl stearate, 4.6%; methyl octadecenoate, 45.3%; methyl octadecadienoate, 42.0%; methyl octadecatrienoate, 8.1%. The methyl esters (46.7 g in 300 ml of methanol) were ozonized as before, the methanol removed from the ozonolysis products *in vacuo,* 300 ml of 90% formic acid added, and the oxidation carried out with a total of 75 ml of 30% hydrogen peroxide. The last step was carried out behind safety shields and in three successive stages, with reflux of the solution for 1 hr after each addition of hydrogen peroxide. After removal of the formic acid by distillation, the product was esterified with methanol (200 ml) in the presence of 2,2-dimethoxypropane (100 ml) with 0.5 ml of concentrated hydrochloric acid as catalyst. The solution was allowed to stand overnight, then distilled to remove solvent. The residue was dissolved in methylene chloride, and the solution washed three times with water. Each wash was backwashed with methylene chloride. The methylene chloride was removed by distillation and the residue distilled through a 8 mm x 60 cm spinning band column. Constants for the major high-boiling fractions are summarized in Table VI. The total composition of the 9–15 carbon diester fractions is summarized in Table VII.

Discussion

One purpose of this paper is to call attention to the potential use of hydrazine as a chemical reactant for

TABLE VI
Distillation of Methyl Esters
8 mm x 60 cm Spinning Band Column
100:1 Reflux Ratio

Compound	Wt, g	Boiling range, C/mm Hg	GLC purity, %	n_D^{30}
Methyl pelargonate	1.55	91– 94/11	99+	1.4181
Dimethyl adipate	0.87	104–108/11	93.1	1.4236
Dimethyl azelate	15.71	139–148/11	99+	1.4320
Dimethyl dodecanedioate	8.53	168–180/11	99+	1.4383
Dimethyl pentadecanedioate	2.77[a]	186–195/11	99+	1.4413 (35C)

[a] An additional 2.96 g was recovered from the column and pot residue.

TABLE VII

Over-all Composition of the 9–15 Carbon Diester Fractions

No. of carbon atoms in dicarboxylic acid	Composition, mole %
9	56.1
10	0.9
11	0.6
12	25.3
13	0.0
14	0.0
15	17.1

fats. Depending on future price and availability of hydrazine, whether premium prices for C_{12} and C_{15} dibasic acids may be merited over those for C_9 acids, and a number of unnamed factors, this process may be worthy of further consideration. At present pilot-plant work may be justified to produce C_{12} and C_{15} dibasic acids in amounts sufficent to evaluate their properties and to determine the demand for them in commercial products, such as polymers, plasticizers, and possibly fibers.

Commercial production of C_{12} dibasic acid has been announced recently, and numerous outlets are anticipated (14). If this dibasic acid and not the C_{15} acid were desired, it would be derived from linoleic acid (3) or from linoleic acid-rich sources in soybean, safflower, and tall oils.

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Investigations on the Side Reactions in Sulfonation Reactions—Hydrophobic Compounds in the Unsulfonated Oil Fraction.

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Abstract

Petroleum ether extracts of alkylbenzene sulfonates prepared by sulfur trioxide, oleum, and sulfuric acid were compared. These extracts contained by-products as well as unreacted material. Dialkylbenzene, originally existing in raw alkylbenzene, resisted against sulfonation, especially when sulfur trioxide was used as sulfonating agent. Sulfone formation seemed to occur in the early stage of sulfonation. Sulfonation with sulfuric acid gave different characteristics to the petroleum ether extract compared with two other means.

Introduction

THE SULFONATION REACTIONS of benzene and its alkyl derivatives have been studied extensively (10,11,12,15,17). The conventional sulfonating agents are oleum, sulfuric acid, and more recent, sulfur trioxide (2,5,6,7,8,9,13,14). These agents have been widely used, however, very little information is available on the by-products formed during the reaction. The known by-products are: sulfonic acid anhydride, dialkylphenyl sulfone, polysulfonates, and other dialkylated compounds (4,6,7,8,9,17). The authors believe that these compounds may seriously influence the sulfonation reaction.

It is the purpose of this paper to report our findings on the by-products, particularly the hydrophobic substances, formed in sulfonation reactions with sulfur trioxide, oleum, and sulfuric acid.

Experimental

Materials and Methods. Alkylbenzene and n-dodecylbenzene were used in the study. Alkylbenzene was a commercial product, Alkane 56, made by Oronite Chemical Co.; n-dodecyl benzene was synthesized in the laboratory from n-dodecanoyl chloride (10). Sulfur trioxide was distilled from 65% oleum. The sulfuric acid reagent was prepared from 22% oleum and 98% sulfuric acid. All solvents used were of reagent grade.

Sulfonation. The sulfonation reactions with sulfur trioxide were carried out as described by Gilbert et al. (7). Gaseous sulfur trioxide, mixed with dry air was bubbled through the sample. Eighteen separate sulfonations were carried out with sulfur trioxide at 40, 50, and 60C, for 1 and 2 hr reaction periods each. One sample each was also sulfonated with oleum and sulfuric acid for comparison with standard process (13). The conditions of the reaction are given in Table I.

Sample Preparation and Extraction. Sulfonic acid anhydride in the resulting reaction medium with sulfur trioxide was decomposed to sulfonic acid by adding 1% of water w/w and the acid was neutralized with 10% NaOH. The hydrophobic substances were then extracted with petroleum ether according to the standard AST method 1568-58T (1).

From the neutralized paste, 1.5–2.0 g of hydrophobic oils were obtained. The degree of reaction was calculated using the following equation:

$$\text{Degree of reaction } \% = \frac{\text{Combined Alkylbenzene}}{\text{Combined Alkylbenzene} + \text{Petroleum ether extract}} \times 100$$

where combined alkylbenzene = active ingredient with Epton's titration method (3,16) $\times \frac{246}{348}$