peroxide is also affected by the acetic acid concentration, being 1.8 in a 5% solution compared with 2.631 in a 20% solution.

The polarity of the solvent also has an effect on the ease with which diphenylcarbohydrazide is oxidized by oxygen. In water, methanol, and ethanol, diphenylcarbohydrazide immediately forms a red solution unless oxygen is rigorously excluded. In these polar solvents, diphenylcarbazone acts as an indicator. It is red only above about pH 6; in more acid solutions, it is light yellow. This probably explains why Glimm et al. (2) were not able to get a Stamm test in ethanol and methanol or with hydrogen peroxide; their reagents may have been contaminated with acid.

The color produced in the Stamm test is not stable and should be read within 30 min. Solutions of diphenylcarbazone in tetrachloroethane are not stable for more than a few hours. According to Krumholtz and Watzek (7), diphenylcarbazone is oxidized by oxygen to the 5-hydroxy-2,3-diphenyl-2H-tetrazolium hydroxide inner salt.

Solutions of fat hydroperoxides in tetrachloroethane are not stable, and the peroxide value should be determined immediately after the solvent is added.

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Application of the Ritter Reaction to Petroselinic Acid

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Abstract

Substituted amidostearic acids were prepared from petroselinic acid by reaction, in the presence of sulfuric acid, with hydrogen cyanide, acetonitrile, propionitrile, acrylonitrile and benzonitrile. The products were crystalline solids. Attempts to obtain monoamides containing a nitrile group by the use of dinitriles were unsuccessful.

Introduction

AMONG THE OILSEED PLANTS selected for further study in the New Crops program of the U. S. Department of Agriculture are several members of the *Umbelliferae* family including parsley (*Petroselinum sp.*), wild carrot (*Daucus carota*), and fennel (*Foeniculum vulgare*). The characteristic fatty acid of the seed oil from these plants is petroselinic (6-octadecenoic) acid, and any industrial utilization of the oils would depend primarily on the petroselinic acid or its derivatives.

One means of modifying petroselinic acid to give potentially useful compounds is by modification at the site of the double bond. The formation of N-substituted amides by interaction of nitriles and olefins in the presence of strong acids, now designated the Ritter reaction, has been studied by numerous investigators (see references 1 and references cited therein) using a variety of nitriles and a variety of olefinic compounds. Many of the products of the Ritter reaction have been stated to be useful in the preparation of plasticizers, polymers, detergents and surface-active materials useful as wetting, emulsifying, or dispersing agents (2–5).

In the course of utilization studies with petroselinic acid, we have carried out its reaction with hydrogen cyanide and a variety of nitriles in the presence of sulfuric acid. This paper is a discussion of this work.

Materials and Methods

The petroselinic acid (6-octadecenoic) was obtained from parsley seed by the method of Fore, Holmes and Bickford (6). The nitriles were purchased from the Eastman Kodak Company and used without further purification. The acetamido-, propioamido-, acrylamido- and benzamidostearic acids were formed by the method of Roe and Swern (7,8), except that the waxy material, which formed in the diluted acid overnight, was separated, dissolved in ethyl ether, the ether solution washed with water to neutrality, dried with sodium sulfate and evaporated under aspirator vacuum at less than 40C to obtain the crude product. The crude product was wastefully recrystallized three times from acetone (1 g to 4–5 ml acetone) at −5C to give the purified products reported in Table I.

The formamidostearic acid was made by suspending two equivalents of powdered sodium cyanide in the petroselinic acid in a large test tube equipped with a stirrer. The sulfuric acid was added dropwise, the temperature of the reaction tube being kept above the melting point of petroselinic acid (31C) but below 40C as the sulfuric acid was added. More difficulty was encountered in crystallizing the formamidostearic acid and a small amount of it was crystallized only once from acetone.

The yields of the crude product and their nitrogen contents; and the analyses, molecular weights and melting points of the purified products are shown in Table I.

Results and Discussion

Roe and Swern (7) applied the Ritter reaction to oleic acid and obtained products which melted over wide ranges. They point out that considerable isomerization occurs in the sulfuric acid medium, resulting in a mixture of many isomers instead of only the two which would be expected if the double bond remained in the 9,10-position throughout. Their products were initially viscous, oily masses, which required as long

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TABLE I

Amidostearic Acids from Petroselinic Acid and Nitriles by the Ritter Reaction [a]

| Derivative | Crude product | | Recrystallized product | | | | | |
	% Yield	% N	% C	% H	% N	% S [b]	M. W.	M. P., °C
Formamido-	82	3.2	....	....	4.08 (4.28)	0.06	......	82–85
Acetamido-	94	3.7	70.11 (70.33)	11.54 (11.51)	4.05 (4.10)	0.36	346 (342)	72–76
Propionamido-	99	3.6	70.49 (70.99)	11.66 (11.62)	3.82 (3.94)	1.06	362 (356)	79–93
Acrylamido-	100	3.8	70.82 (71.34)	11.52 (11.12)	3.89 (3.96)	0.56	372 (353)	78–86
Benzamido-	c	c	73.44 (74.39)	10.38 (10.24)	3.40 (3.47)	0.37	410 (404)	117–126

[a] Elemental analyses and molecular weights by Galbraith Laboratories; the calculated values are in parentheses.
[b] The pure compound should contain no sulfur.
[c] Contaminated with benzonitrile.

as 24 hr to solidify even when stirred with water to insure rapid removal of sulfuric acid. They suggest, therefore, that the initial stabilized reaction product has the structure,

$$CH_3(CH_2)_x \, CH(CH_2)_y \, COOH$$
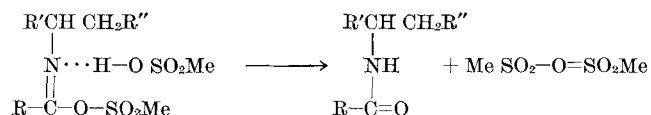$$|$$
$$N$$
$$||$$
$$R-C-O-SO_3H \qquad I$$
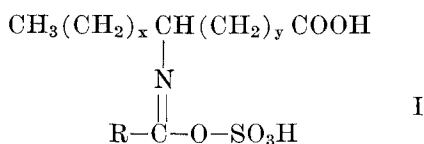
and requires time to hydrolyze and tautomerize to the N-substituted amide actually isolated. In one instance, they showed (7) that the crude N-substituted acetamide isolated from their experiments had no sulfur-containing materials remaining after it was washed free of sulfuric acid.

The products presented in Table I from petroselinic acid and various nitriles also crystallized very slowly after the reaction mixture was poured over ice. These materials were all allowed to crystallize in the aqueous reaction mixture before being taken up in ether and treated as described in the preceding section. However, to see whether a lengthy hydrolysis was necessary to yield the amides, the oily material from one experiment using petroselinic acid and acetonitrile was extracted into ether immediately after the reaction mixture was poured over ice. The ether solution was washed free of sulfuric acid and dried over sodium sulfate (35 min elapsed between the time the mixture was poured onto crushed ice and its being obtained in a dry ether solution). Evaporation of the ether left a residue which crystallized to give a nearly identical yield of crude acetamidostearic acid to that reported in Table I where the crude amide was allowed to crystallize overnight in contact with the aqueous reaction mixture.

Thus, though analogous materials to I are normally considered to be intermediates in the Ritter reaction (1,7,9), it is clear from the experiment described above that if such a material is present in the original reaction mixture, it is rapidly hydrolyzed when this mixture is mixed with water. In fact, from the results of Clarke et al. (1), it appears that such an intermediate does not persist very long even in the sulfuric acid reaction mixture before mixing with water. They carried out two experiments employing acetonitrile and 1-dodecene, and designed to yield the sulfate ester analogous to I. In one of them, 100% sulfuric acid was used to effect the Ritter reaction and in the other methanesulfonic acid was used to rigorously exclude the possibility of water which might hydrolyze the sulfate ester. In both cases the product was the nor-

mal Ritter product, N-(2-dodecyl) acetamide. They did not attempt an explanation. However, it should be pointed out that unreacted sulfuric acid, or even methanesulfonic acid, can furnish a proton to the nitrogen of the sulfate ester and allow analogues of I to decompose to the amide as pictured below without the necessity of water being present:

$$\begin{array}{ccc} R'CH\ CH_2R'' & & R'CH\ CH_2R'' \\ | & & | \\ N\cdots H-O\ SO_2Me & \longrightarrow & NH \quad + Me\ SO_2-O=SO_2Me \\ || & & | \\ R-C-O-SO_2Me & & R-C=O \end{array}$$

In contrast to the fact that the products of Roe and Swern (7) apparently were free of sulfur-containing compounds, our crude products invariably gave a positive analysis for sulfur. The products were not completely freed of the sulfur-containing impurity, of impurities by several recrystallizations (see Table I). Most investigators of the Ritter reaction do not mention analysis for sulfur in their work, but Clarke et al. (1) did isolate a sulfur-containing material in one of their experiments. They considered it to be a sulfonate since it was not hydrolyzed by refluxing for 3 hr in 10% sulfuric acid. The nature of the sulfur-containing impurities in our products was not investigated.

In our work, brief attempts were made at preparing monoamides containing a nitrile group. Reactions of petroselinic acid (1 mole) with malononitrile (3 moles) or succinonitrile gave oily materials which would not crystallize. These materials probably were mixtures of the mono- and diamides similar to those reported by Roe and Swern (7) in their work with oleic acid, though they obtained crystalline solids. The formation of such mixtures is not unexpected in view of the fact that other investigators (10,11) have obtained fair to good yields of diamides by using one mole of dinitrile to two moles of olefin in the Ritter reaction.

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