

Further Studies on Methanesulfonic Acid Catalyzed Additions to Oleic Acid¹

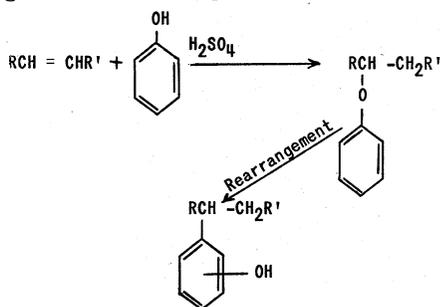
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Abstract

Infrared study of the products of the addition of *m*-cresol to oleic acid in methanesulfonic acid, revealed the presence of both the *m*-cresoxy and hydroxytolyl substituted stearic acids. By employing a modified extractive procedure to recover the products of the reaction, followed by chromatography on a Florisil column, a separation of the two types of addition products was effected.

The methanesulfonic acid catalyzed addition reaction was extended to include aryl thiols. Among the sulfur analogues of the previously used phenols that were added are: benzenethiol, *p*-*t*-butylbenzenethiol, 2-naphthalenethiol, *o*-, *m*-, and *p*-toluenethiol. The yields of addition products (which were unobtainable in sulfuric acid media) ranged from 37–70%. In contrast with the results obtained when phenolic nucleophiles were employed no evidence for the formation of rearranged addition products has been found. Thioethers were the only products identified.

PREVIOUS investigators, notably Niederl and his co-workers (3,4,5) have proposed that the addition of a phenol to an olefin in sulfuric acid media proceeds via an intermediate which subsequently rearranges according to the following reaction equation:



On the occasions when *m*-cresol was added to oleic acid in sulfuric acid medium Niederl (5,6) did not isolate any of the *m*-cresoxy stearic acid intermediate, but obtained the rearranged isomeric (2-hydroxy-4-methyl-phenyl) stearic acid.

In a previous report from this laboratory (1) data were presented showing improvement in yields of products when methanesulfonic acid was used in place of sulfuric acid (2) as catalyst-solvent for the addition of phenols and phenyl ethers to oleic acid. Included in the group of phenolic nucleophiles that gave good yields of addition products was *m*-cresol.

The procedure employed specified that the reaction mix be poured into ice-water at the conclusion of the reaction period and the addition product extracted from the resulting admixture. The recovered product after esterification with methanol had values for sa-

ponification equivalent and % hydroxyl which agreed well with the theoretical values for the rearranged product i.e., the methyl ester of hydroxytolylstearic acid.

A procedure for isolating the addition product by a method that would permit recovery of the expensive methanesulfonic acid catalyst-solvent for re-use seemed quite desirable. During investigation of an extractive procedure for recovery of the *m*-cresol-oleic acid addition product, evidence was obtained for the presence of a *m*-cresoxy stearic acid intermediate in the recovered products.

By modifying the recovery procedure, products are obtained which differ from those obtained formerly. If the reaction mixture is extracted prior to dilution, and the methanesulfonic acid re-used in subsequent runs, the unrearranged products are recovered from the extracts. The methanol esterified products upon analysis had saponification equivalents which agree with theory for a proper addition product. The % hydroxyl, however, is much lower than that required for theory. Infrared examination of the material shows a high degree of absorption in the 1100–1300 cm^{-1} region characteristic of ethers. Absorption present in the 3300–3700 cm^{-1} region indicated the presence of free hydroxyl groups. These results suggest that the material is a mixture of esters of *m*-cresoxy and hydroxytolyl stearic acids.

Because the *m*-cresoxy ester is less polar than the ester containing free phenolic hydroxy groups, separation of the mixture by chromatography on a Florisil column was attempted. The early fractions that were eluted from the column, when examined by infrared, showed no absorption peaks in the 3300–3700 cm^{-1} region indicating the absence of free hydroxyl group. The same fractions had strong absorption in the 1100–1300 cm^{-1} region (ether). The fractions obtained from later elutions with solvents of increased polarity did have hydroxyl absorption and a considerable lessening of the ether absorption.

By treatment with dilute acid, the *m*-cresoxy derivative obtained from the early fractions could be rearranged to the hydroxytolyl ester. This was proven by infrared examination of the product, i.e., appearance of the OH absorption peaks in the 3300–3700 cm^{-1} region.

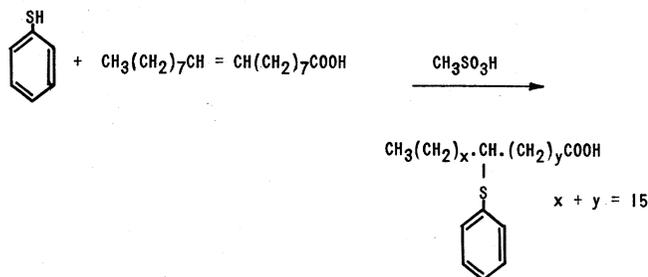
The success obtained with the use of methanesulfonic acid as catalyst-solvent for the addition of phenols and phenyl ethers to oleic acid prompted an extension of the reaction to aryl thiols and thio ethers. Roe *et al.* (2) had indifferent success when they attempted to add benzenethiol to oleic acid using sulfuric acid as the catalyst. However, this was not true when we employed methanesulfonic acid for that purpose. A number of sulfur analogues of the previously used phenols were successfully added. The results of these additions, as well as those obtained with other thiol nucleophiles, are summarized in Table I.

Initially the addition of the thiols proceeds in the same manner as with the phenols but no rearrange-

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ment of the initial addition product takes place. Invariably the end product of the reaction is a thioether. The reaction may be represented as follows:



Experimental

Isolation of m-Cresoxy Substituted Methylstearate. A mixture of 28.2 g (0.1 mol) of oleic acid and 43.2 g (0.4 mol) of m-cresol was added slowly, with rapid stirring, to a flask containing 60 g (0.624 mol) of methanesulfonic acid. Only a slight exotherm was encountered and no external cooling was required. Stirring of the reaction mixture was continued for 6 hr. The reaction mixture was extracted 3 times with 150 ml portions of commercial hexane. The methanesulfonic acid layer was saved for further use. The extracts were combined and washed with water to remove any acid (Extract I).

A second mixture of 28.2 g of oleic acid and 43.2 g of m-cresol was added with stirring to the methanesulfonic acid recovered from the previous run. Again the stirring was continued for 6 hr. At the conclu-

sion of this period, the reaction mixture was extracted with commercial hexane as above. Combining the extracts and water washing yielded Extract II.

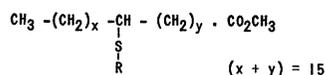
The extracts, I and II, were evaporated to remove solvent and each residue was converted to methyl esters by conventional esterification methods with absolute methanol. Fractionating the methyl esters from Extract I yielded 12.2 g of a product which had a S.E. of 407 and 4.16% OH. Theory for the methyl ester of the hydroxytolyl substituted stearic acid S.E. 405, % OH 4.20, yield 30%. Fractionation of the methyl esters of Extract II yielded 28 g of product which had a S.E. of 410 and 2.95% OH, yield 69%. The low hydroxyl content of the esters from Extract II show that it is a mixture of the isomeric m-cresoxy and hydroxytolyl derivatives since the theoretical hydroxyl content for the rearranged product is 4.20%.

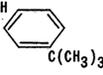
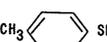
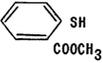
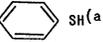
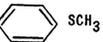
To separate the isomers chromatographically, Florisil was used as the adsorbent. Employing a 30 to 1 ratio of adsorbent to material, 7.18 g of the mixed esters from Extract II in 75 ml of hexane were charged on to a 216 g Florisil column. Elution with hexane removed 2.43 g of material which when examined by I.R. showed strong absorption at 1100–1300 cm^{-1} (ether) and no absorption in the 3300–3700 cm^{-1} region (absence of OH). The non-hydroxy material could be rearranged to the hydroxy derivative by treatment with dilute methanesulfonic acid.

Further elution with 20:80 benzene-hexane mixture, followed by elution with methylene chloride, removed 3.71 of material from the column. This product under I.R. had strong absorption at 3300–3700 cm^{-1} , indicat-

TABLE I

Methyl Esters of Arylthio Stearic Acids



RSH	Boiling Range		Yield %	Saponification Equivalent		Carbon %		Hydrogen %		Sulfur %	
	°C	mm		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
 SH	170-195	0.1	60	407	385	73.83	73.73	10.41	10.43	7.88	8.10
 SH C(CH ₃) ₃	Molecularly Distilled		70	463	450	75.26	74.56	10.89	10.74	6.93	7.09
 SH CH ₃	170-205	0.1	37	421	378	74.23	73.62	10.54	10.73	7.62	8.66
 SH CH ₃	185-207	0.1	63	421	388	74.23	74.31	10.54	10.76	7.62	7.54
 CH ₃ SH	170-205	0.1	52	421	394	74.23	74.07	10.54	10.65	7.62	7.49
 SH	Molecularly Distilled		48	457	440	76.03	76.26	9.71	9.74	7.02	7.01
 SH COOCH ₃	Molecularly Distilled		40	232	229	69.78	69.50	9.54	9.66	6.90	6.83
 SH (a) Cl	Molecularly Distilled		37	441	431	68.07	67.86	9.37	9.38	7.27	7.17
 SCH ₃	No addition product		—	—	—	—	—	—	—	—	—
HS.CH ₂ .CH ₂ .COO(C ₈ H ₁₇)	Molecularly Distilled		—	257 ^(b) 208 ^(c)	212	69.98 ^(b) 66.30 ^(c)	67.50	11.36 ^(b) 10.64 ^(c)	11.12	6.23 ^(b) 7.70 ^(c)	7.54

(a) Analysis of product for chlorine calc. 8.04%, found 8.19%.
 (b) Calculated as mixed methyl and isoocetyl ester.
 (c) Calculated as dimethyl ester.

ing it to be the hydroxytolyl product. The ratio of hydroxy to non-hydroxy (ether) product in the mixture is about 3:2.

Addition of Thiols to Oleic Acid. The same procedure used for obtaining the addition products with phenolic nucleophiles was employed (1). The molar ratio of methanesulfonic acid to oleic acid was always the same (6:1). However, because of the limited amount of thiol available, the ratio of nucleophile to oleic acid was reduced from 4:1 to 2:1 in several instances. In all the experiments the excess of thiol was recovered with the reaction product. Titration of the products with ethanolic iodine solution gave negative results, demonstrating the absence of free mercapto groups. The yields and analyses of the resulting thioethers are summarized in Table I.

Results and Discussion

The superiority of methanesulfonic acid over sulfuric acid as catalyst-solvent for addition to oleic acid is demonstrated again by the yields of thioethers resulting from the thiol additions. It was even possible to add polycyclic thiols such as 2-naphthalenethiol. Previous investigators using sulfuric acid for the addition of thiols experienced difficulty in isolating the products. The advantage in using methanesulfonic acid is probably due to the lesser tendency for oxidation and other undesirable side reactions to take place in this medium. The negative ethanolic iodine titrations indicate the products to be thioethers exclusively. Rearrangements of thioethers similar to those of the phenolic addition products would yield titratable free mercapto (-SH) groups.

The inclusion of thioanisole in Table I serves to demonstrate that thioethers do not add to oleic acid. This result is not unexpected since the products isolated from thiol addition were thioethers. It will be recalled that phenolic ethers such as anisole and phenetole could be added successfully under similar conditions.

The yield of thiol addition products seems to parallel those obtained from their phenolic counterparts. Steric influences of substituents already present in the aromatic ring play a similar role in influencing the yields, i.e., lower yields from ortho substituted compounds; higher yields with meta and para derivatives. Without exception, the odor of the thioether is less disagreeable than the thiol starting material. No yield data are listed in Table I for the experiment when isooctyl 3-mercaptopropionate was added to oleic acid. About 20 g of a distillate was obtained from a fractionation of the ester. The saponification equivalent and elemental analysis of one fraction gave results that lie between the theoretical values for a mixed isooctyl methyl ester addition product and the dimethyl ester addition product. It may be inferred that the values obtained are due to a partial alcoholysis of the isooctyl group during the esterification of the substituted stearic acid.

In addition to the thiols listed in Table I, two additional sulfur derivatives were added to oleic acid: α, α' dimercapto p-xylene $\text{HSCH}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{SH}$ and phenylmercaptoacetic acid (carboxythioanisole). The dimercaptoxylylene added to give a mixture of high mol wt compounds which were unidentifiable. The phenylmercaptoacetic acid was added via the carboxyl group. This type of addition is to be the subject of a future communication.

Acknowledgment

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