

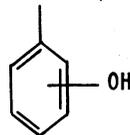
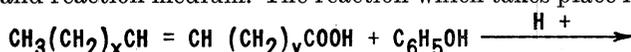
Improved Yields in the Acid Catalyzed Addition of Phenols and Phenyl Ethers to Oleic Acid¹

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Phenols may be added to oleic acid in methanesulfonic acid solution to give the corresponding hydroxyphenylstearates in good yield. With phenol not only is the yield (ca 80%) better than that reported previously using other reagents but considerably less color is developed also. Surprisingly good yields (35–60%) were obtained with such complex phenols as *p*-*t*-butylcatechol and 2-naphthol.

REACTIONS involving additions to a double bond in the aliphatic chain of fatty acids have played a prominent role in the research program of this laboratory (1,5). In one of the papers (6), Roe, *et al.* have described work on the acid catalyzed addition of phenols and phenyl ethers to oleic acid. Although they succeeded in preparing a number of the desired derivatives, by-product formation during the reaction resulted in low yields and highly colored products which were difficult to purify. This paper reports the results of experiments on the addition of phenols and phenyl ethers to oleic acid using polyphosphoric acid or preferably methanesulfonic acid as a catalyst and reaction medium. The reaction which takes place is



where $x + y = 14$

and

$a + b = 15$

As noted above, the use of sulfuric acid as a condensing agent to bring about additions to double

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bonds frequently gives low yields because of polymerization, sulfonation, oxidation, or other undesired reactions. Moreover product color is frequently poor. Roe, *et al.* (6) attempted to obviate this difficulty by the use of a catalyst consisting of a sulfonic acid cation-exchange resin. Actually this resulted in increased yield of desired product in one case, and decreased yield in two cases. To circumvent this difficulty other nonoxidizing acids were tried, such as hydrochloric, phosphoric, mixtures of phosphoric and hydrochloric acids, polyphosphoric acid and methanesulfonic acid. Results were not uniformly successful. In one experiment with phenol using concentrated hydrochloric acid as the catalyst, and maintaining the reaction mixture at steam bath temperature for 6 hr, some evidence of the formation of a small amount of addition product was obtained.

It was found that polyphosphoric acid could also be utilized as a catalyst for some additions. For example, phenetole was successfully added to oleic acid at room temperature, using polyphosphoric acid as the catalyst. A 25% yield of the methyl ester of the addition product was obtained on fractionation of the products of the reaction. The isolated methyl ester had a saponification equivalent of 399 (theory, 419).

For best results, methanesulfonic acid must be present in at least a 6–1 molar ratio to oleic acid. Lower ratios have invariably led to lower yields. Results are summarized in Table I.

Experimental

Starting Materials. Oleic acid (98+%) essentially free of polyunsaturated acids and containing not more than 1.0% saturated acids was used. The phenols, phenyl ethers, and acids were the best commercial grades obtainable and were used as received.

TABLE I
Methyl Esters of Substituted Phenylstearic Acids
 $\text{CH}_3-(\text{CH}_2)_x-\text{CH}(\text{CH}_2)_y\text{CO}_2\text{CH}_3$

R (x + y = 15)

| R ^a | Temperature of reaction | Distillate | | | Residue | | | Theory | | N ^{BD} |
|----------------|-------------------------|---------------|--------------------|--------------------|--------------|--------------|-------------|---------------|--------------|-----------------|
| | | % Yield | % OH | Sap. Equiv. | % Yield | % OH | Sap. Equiv. | % OH | Sap. Equiv. | |
| | Room Room | Not distilled | | | 71.6 83.3 | 4.15 4.33 | 352 386 | 4.35 | 391 | 1.4921 |
| | Room | 32.7 | 3.56 | 428 | 27.5 | | 375 | 3.86 | 440 | |
| | Room Room | 54.2 69.0 | 4.26 4.60 | 398 393 | 21.3 22.1 | 3.1 3.6 | 400 399 | 4.20 | 405 | 1.4860 |
| | Room Steam bath | 39.8 47.5 | | 380 400 | 25.9 31.4 | | 354 900 | | 405 | 1.4782 |
| | Room | 44.9 | | 417 | 25.5 | | 490 | | 419 | 1.4812 |
| | Room | 54.8 | ^b | ^b | | | | | | 1.4925 |

^a The formulas shown are intended only to indicate the radical attached and not necessarily the point of attachment.

^b Could not be determined either colorimetrically or potentiometrically; carbon, % found, 75.4, theory, 75.3; hydrogen, % found, 11.0, theory 10.9.

Preparation of Methyl Esters of Substituted Phenylstearic Acids. For the preparation of the substituted phenylstearic acid esters, a modification of the procedure used by Roe, Parker, and Swern (6) was employed. Typical of these preparations is the one using m-cresol as the added phenol. A mixture of 28.2 g (0.1 mole) of oleic acid and 43.2 g (0.4 mole) of m-cresol was added slowly, with rapid stirring, to a flask containing 60 g (0.624 mole) of methanesulfonic acid. As only a very slight exotherm was observed, no external cooling was necessary. Stirring of the reaction mixture was continued for 6 hr. At the conclusion of this period, the contents of the reaction flask were poured on to cracked ice. After standing overnight, the organic layer was extracted with ether and the ether solution freed of acid by washing with 20% aqueous sodium sulfate solution. The ether extract, after drying over anhydrous sodium sulfate, was evaporatively distilled. The excess of m-cresol in the residue was removed by reduced pressure distillation. The resulting crude substituted stearic acid was esterified by adding 40 ml of absolute methanol, 0.8 g of p-toluenesulfonic acid, and refluxing the mixture for 8 hr. After washing out the catalyst the ester was recovered in the usual manner. The crude ester was vacuum fractionated using a flask equipped with an alembic head. The fraction boiling between 165–205C (mostly 199–203C) at 0.08 mm was the main product. The weight of the fraction was 28 g (69% yield).

In the preparation of the 2-naphthol addition product, the excess of naphthol was not removed prior to esterification.

Results and Discussion

None of the inorganic acids which were tried gave results comparable to those reported by Roe, *et al.* (6) when using sulfuric acid. With polyphosphoric acid, even when a moderately good yield was obtained, difficulties were experienced in washing and isolating the products. With methanesulfonic acid, however, much better results were obtained. By the use of this solvent-catalyst for adding phenol to oleic acid, not only were good yields of reasonably pure products obtained, but the product color was so satisfactory that purification by distillation seemed unnecessary. Generally satisfactory yields were obtained also with m-cresol, phenetole, anisole, and t-butylcatechol. With these compounds, yields were two to four fold those previously obtained with sulfuric acid. Moreover, by use of methanesulfonic acid catalysis, β -naphthol and nonylphenol have been added to oleic acid.

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