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# Addition of Aromatic Compounds to Oleic Acid Catalyzed by Heterogeneous Acid Catalysts

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## ABSTRACT

The addition of aromatic compounds to the double bond of oleic acid was studied using solid acid catalysts. For example, in the presence of an acid clay catalyst (bentonite), phenol reacted with oleic acid to yield 96% of an alkylphenol addition product. When toluene was used as the aromatic reactant, however, the yield of alkylbenzene addition product was less than 2%. In this instance, the major reactions observed were elaidinization and migration of the double bond of oleic acid. The addition of phenol to oleic acid in greater than 95% yield also was accomplished with the use of a sulfonic acid ion-exchange resin catalyst. This same catalyst also catalyzed the addition of toluene and benzene to oleic acid to yield 82% and 22%, respectively, of alkylbenzene-type addition products. In the latter instances, the major side product formed was γ-stearolactone. Capillary gas chromatographic (GC) analyses of the alkylbenzene addition products obtained showed them to be mixtures of positional isomers. The isomer distributions were subsequently determined by GC-mass spectrometry (MS).


## INTRODUCTION

The addition of aromatic compounds to oleic acid has been studied using various types of Lewis and Bronsted acids as catalysts (1,2). Eisner et al. (3-5) reported that methanesulfonic acid was the preferred acid catalyst for the addition reaction of aromatic compounds to oleic acid because this acid gave not only good yields of addition products, but products with less color. Recently, Nakano et al. (6) identified all of the reaction products formed when aromatic compounds are reacted with oleic acid in the presence of methanesulfonic acid and proposed a reaction pathway to account for the products identified.

Whereas methanesulfonic acid gives good yields of addition products, the use of this acid catalyst has the following disadvantages: (a) high ratios of methanesulfonic acid to oleic acid are needed to obtain good conversion to product; (b) this catalyst is difficult to remove from the reaction mixture; (c) purifying the catalyst before recycling is necessary; (d) the acid is volatile ($bp_{10}$, 167 C) and has corrosive properties.

Solid acid catalysts, therefore, would be preferred to overcome these disadvantages. Accordingly, 2 types of solid acid catalysts were studied, an acid clay and a strong acid ion-exchange resin. The addition reaction of phenols to oleic acid in the presence of a clay catalyst has been reported by Barrett et al. (7). However, yields were not specified, none of the by-products were identified and other aromatic compounds were not studied. The addition reaction of phenols and phenylethers to oleic acid in the presence of a sulfonic acid ion-exchange resin was reported by Roe et al. (2). In this instance, the yields of addition products were not good (<40%), and the by-products were not identified.

The present study was undertaken to identify the reaction products formed when aromatic compounds are reacted with oleic acid in the presence of heterogeneous acid catalysts, and to determine the isomer distribution of the alkylbenzene derivative products obtained from these reactions.

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## EXPERIMENTAL

### Materials

Oleic acid (98%) was obtained from Applied Science Laboratories (State College, PA). Clay (Clarolite T-300) was purchased from Georgia Kaolin Company (Elizabeth, NJ). The strong acid ion-exchange resin (Amberlyst-15) was purchased from Rohm and Haas Company (Philadelphia, PA). All other reagents were used as received from chemical suppliers.

Gas liquid chromatography (GLC) was conducted with a Perkin-Elmer Sigma 3 gas chromatograph equipped with flame ionization detectors (FID). Separations were obtained on a 15 m capillary column coated with methyl silicone fluid. Thin layer chromatography (TLC) was performed on Silica gel G plates (250 μ) obtained from Analtech (Newark, DE). Plates were developed with toluene/ether (94:6) and visualization was accomplished by spraying the plates with 5% cupric acetate in 20% phosphoric acid, then charring. A Perkin-Elmer model 720B infrared (IR) spectrophotometer was used for IR analysis. Mass spectra (MS) were obtained on a Hewlett-Packard model 5995 GC-MS instrument. Column chromatography was carried out on Silica gel 60 A (75-150 μ) using hexane/methylene chloride gradients as the eluant. Fractions (100 mL) from the column were monitored by TLC.

### Reaction Procedures

*Method A: clay catalyst.* The preparation of hydroxyphenylstearic acid is a typical example. A mixture of oleic acid (84.6 g, 0.30 mol) and phenol (56.4 g, 0.60 mol) was introduced into a 1 L autoclave and the acid clay (2.54 g, 3 wt % to oleic acid) was added. The autoclave was purged with nitrogen and the contents heated to 160 ± 5 C, for 4 hr (maximum pressure 100 psi). The reaction products were esterified by $BF_3$-$CH_3OH$ reagent, then separated by column chromatography. The isolated products were derivatized to silylethers by N-trimethylsilylimidazole (TMSI) (8), then analyzed by capillary GC. Product identification was made by GC-MS comparison with authentic compounds as previously described (6).

*Method B: strong acid ion-exchange resin.* The resin (Amberlyst-15) was washed with 5% $H_2SO_4$, 4 times, washed with distilled water until the pH was neutral, air dried overnight and then heated for 7 hr at 100 C under vacuum (10 mm Hg). The acidity of the dried resin was determined by tritration with 0.1 N normal sodium hydroxide. The concentration of sulfonic acid groups on the resin was 4.3 mmol/g resin.

The dry resin (0.43 g, 1.85 mmol of sulfonic acid groups) was placed into a 50 mL round-bottom flask equipped with thermometer, condenser and magnetic stirring bar. A mixture of oleic acid (4.17 g, 14.8 mmol) and phenol (2.78 g, 29.6 mmol) was added to the flask, the contents heated to 110 ± 2 C and this temperature maintained for 8 hr. The reaction mixture was purified and analyzed as in method A.

## RESULTS AND DISCUSSION

When phenol is reacted with oleic acid in the presence of a solid acid clay catalyst, 2 types of addition products are found in the early stages of the reaction. One product is alkylphenol 2 (Fig. 1) and the other is phenylether product 3. As the reaction proceeded, phenylether product 3 decreased and alkylphenol 2 was the only product observed in the final stage of the reaction. This same phenomenon, as well as the rearrangement pathway, was reported previously in the reaction catalyzed by methanesulfonic acid (6).

At a temperature of 160 C and a 4 hr reaction time, phenol gave 96% of alkylphenol product 2, whereas toluene gave less than 2% of alkylbenzene product 2. In this latter instance, the major reactions observed were elaidinization and migration of the double bond of oleic acid. The lower reactivity of toluene in this clay-catalyzed reaction might be caused either by the clay's low acidity (the strongest acid site observed is $0.8 < H_0 < 4.6$ [9]), the lower reactivity of toluene than phenol or poorer adsorptivity of toluene on the clay surface. Capillary GC analysis and IR spectroscopy of phenol addition product 2 showed that the orientation of the hydroxyl group in the alkylphenol product 2 favored the ortho isomer over the para isomer by 2:1. This result suggests that the adsorption of phenol onto the clay surface is an important step for subsequent reaction with oleic acid because in homogeneous reactions, the para isomer is favored (6).

In order to study the effect of catalyst acidity, a strong acid ion-exchange resin was studied. This catalyst was found to have no catalytic activity without drying (10). The resin showed good catalytic activity however after it was dried at 100 C for 7 hr under vacuum (10 mm Hg). As with the clay catalyst in the early stages of the reaction, ca. 10% of phenylether product 3 was formed. This product decreased with the increasing reaction time until no phenylether product 3 was present after 8 hr, at which time the yield of alkylphenol product 2 exceeded 93%, when a ratio of sulfonic acid groups on the resin-to-oleic acid of 1:8 was used. Higher ratios (1:4) were unnecessary and a lower ratio of 1:16 resulted in incomplete reaction (Table I).

Compared with the clay, the resin has 2 advantages. The resin can catalyze the addition reaction at lower temperature and atmospheric pressure; however, a disadvantage is the requirement of a longer reaction time, 8 hr rather than 4 hr.

When toluene was used as the aromatic reactant, γ-stearolactone 4 (Fig. 2) was formed as a major by-product. At a temperature of 110 C and after 20 hr reaction time, the yield of tolylstearic acid (alkylbenzene product) 5 was 82% and γ-stearolactone 4 was 6%. In the early stages of the reaction, tolylstearic acid 5 and γ-stearolactone 4 are formed in a constant ratio of ca. 2:1. After the conversion of oleic acid reaches ca. 80%, the γ-stearolactone is converted to tolylstearic acid. Two possibilities may account for this observation. The first is that γ-stearolactone 4 reacts directly with toluene to yield tolylstearic acid 5. The second is that γ-stearolactone is initially converted back to a carbocation and then reacts with toluene to form the tolylstearic acid product (Fig. 2).

To clarify this point, we prepared tolylstearic acid 5 directly from γ-stearolactone and compared its composition with tolylstearic acid obtained from oleic acid. The alkylbenzene addition products obtained are a mixture of positional isomers, which are separable by capillary GC (Fig. 3). Comparing the isomer distribution in the tolylstearic acid product obtained from oleic acid with that obtained from γ-stearolactone, we found that the isomer distribution was very similar. This result indicates that γ-stearolactone 4 does not react directly with toluene, but suggests that γ-stearolactone and oleic acid are both converted to the same isomeric mixture of carbocation intermediates, which react with toluene to form tolylstearic acid 5 (Fig. 2). This result also suggests that the migration of the carbocation along the alkyl chain of oleic acid is rapid compared with its reaction with toluene.

The addition reaction of aromatics to oleic acid seems to depend on the electron density of the aromatic ring. The yields of addition products obtained using different aromatic reactants in the presence of the resin catalyst are

**TABLE I**

**Phenol Addition to Oleic Acid Catalyzed by Resin**

| Sulfonic acid group[a] | Phenol[a] | Yield of alkylphenol[b] (%) | |
|---|---|---|---|
| Oleic acid | Oleic acid | 4 hr | 8 hr |
| 1/2 | 4 | 91 | 95 |
| | 4 | 77[c] | 91[c] |
| 1/8 | 4 | 76 | 93 |
| | 2 | 79 | 94 |
| 1/16 | 2 | 47 | 63[d] |

[a]Molar ratio.
[b]Reaction temperature 110 C.
[c]Reaction temperature 80 C.
[d]Twenty hr reaction; 83% yield.

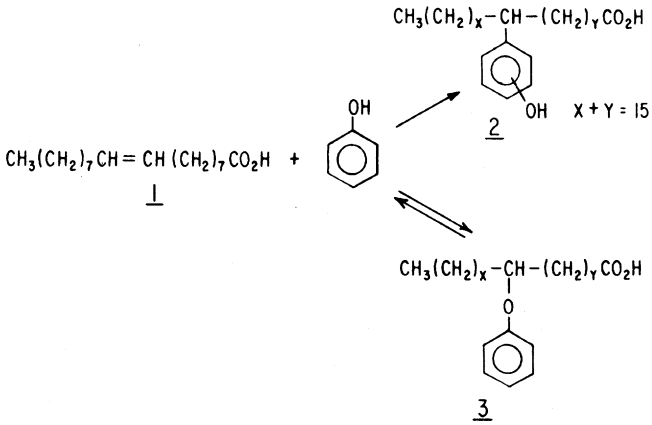


**FIG. 1. Scheme for reaction of oleic acid with phenol.**

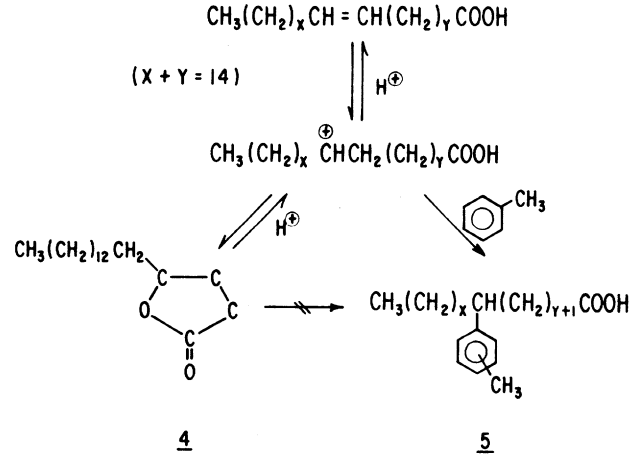


**FIG. 2. Scheme for reaction of oleic acid with toluene and γ-stearolactone.**

summarized in Table II. Because the aromatic compound also acts as solvent, the more polar the aromatic the better it stabilizes the carbocation intermediate. The rate in going from oleic acid to γ-stearolactone also seems to depend in part on the polarity of the aromatic compound.

Positional isomers of phenylstearic acid (the alkylbenzene product of oleic acid with benzene) were separated into 5 peaks by capillary GC (Fig. 4). Each of the 5 peaks was subsequently analyzed by GC-MS to determine its isomer composition. The results of MS analysis of peak 4 are shown in Figure 5. From this analysis, peak 4 was identified as being the 16-phenylstearic acid derivative. The latter isomer arises from addition of benzene to oleic acid when the carbocation is at the ω-2 position of the alkyl chain. The distribution of positional isomers of phenylstearate for the 5 peaks shown in Figure 4 is summarized in Table III. According to the results from GC-MS analysis, the addition compound is a mixture of positional isomers with the phenyl substituent located from the C 3 (β) to C 17 (ω-1) positions of the alkyl chain. Peak 1 is composed of the C 3 to C 13 isomers and the C 14, C 15, C 16 and C 17 isomers are peaks 2-5, respectively.

A positional isomer distribution of phenylstearic acid obtained using $AlCl_3$ as catalyst has been reported previously by Smith et al. (11-13). They demonstrated by means of a $CrO_3$ oxidation procedure that the phenylstearic acid obtained was a mixture of positional isomers with the phenyl substituent located at the $C_6$ to $C_{17}$ positions of the hydrocarbon chain. Their results do not agree with our results, probably because of the less accurate methodology used by them. Accordingly, 3 types of phenylstearic acid were prepared using different acid catalysts (Table III). The catalysts used were the sulfonic acid ion-exchange resin, methanesulfonic acid (6) and $AlCl_3$ (12). No significant difference in positional isomer distribution was found in the phenylstearic acid products obtained using the 3 different catalysts. This indicates that the reaction pathway leading to addition product is similar for the 3 acid catalysts.

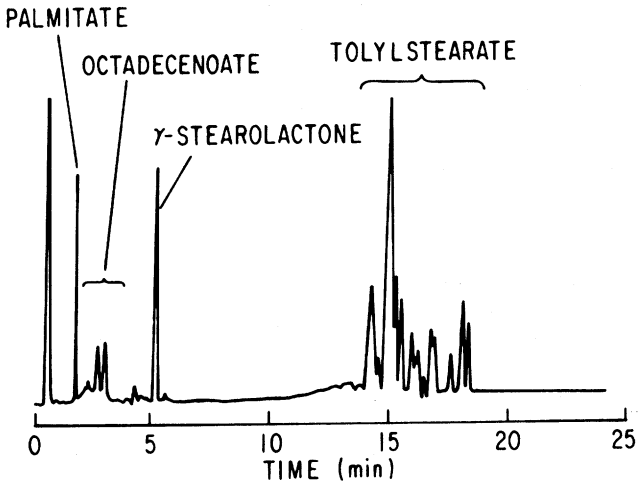


**FIG. 3. Capillary GC of reaction product mixture of oleic acid and toluene.**

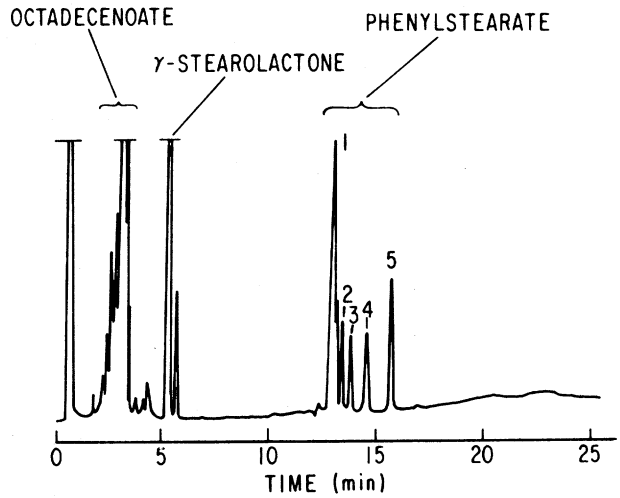


**FIG. 4. Capillary GC of reaction product mixture of oleic acid and benzene.**

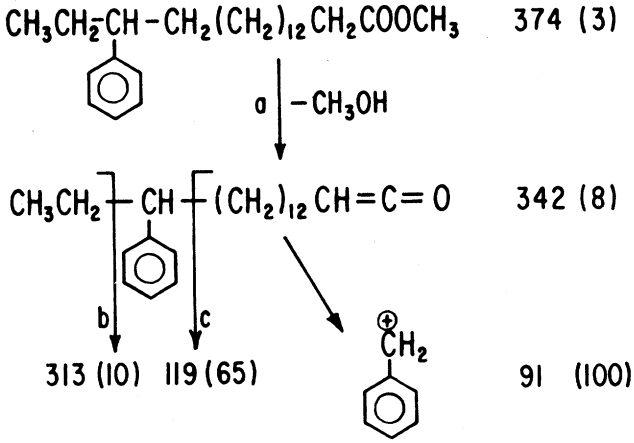


**FIG. 5. MS fragmentation pattern for methylphenylstearate isomers, peak 4, Figure 4.**

**TABLE II**

**Aromatics Addition Catalyzed by Resin[a]**

| Aromatic | Phenol | | Toluene | | Benzene | |
|---|---|---|---|---|---|---|
| Reaction temperature (°C) | 80 | 110 | 110 | | 80 | |
| Reaction time (hr) | 8 | 8 | 8 | 20 | 8 | 60 |
| Product (%) | | | | | | |
| Octadecenoic acid | 4 | 0 | 5 | 8 | 87 | 42 |
| γ-Stearolactone | 0 | 0 | 20 | 6 | 1 | 25 |
| Alkylbenzene | 91 | 95 | 66 | 82 | 2 | 22 |

[a]Molar ratio; oleic acid/aromatics/sulfonic acid group on resin = 2/8/1.

**TABLE III**

**Isomer Distribution in Methylphenylstearate by GC-MS**

| GC peak number | Isomer | Distribution (%) Resin | $CH_3SO_3H$ | $AlCl_3$ |
|---|---|---|---|---|
| 1 (mixture) | C-3 to C-13 | 50 | 62 | 62 |
| 2 (mixture)[a] | C-14 | 10 | 8 | 8 |
| 3 | C-15 | 8 | 6 | 8 |
| 4 | C-16 | 12 | 9 | 8 |
| 5 | C-17 | 20 | 15 | 14 |

[a]Contains minor amount of C 13 isomer.

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REFERENCES

1. Stirton, A.J., B.B. Schaeffer, A.A. Stawitzke, J.K. Weil and W.C. Ault, JAOCS 25:365 (1948).
2. Roe, E.T., W.E. Parker and D. Swern, JAOCS 36:656 (1959).
3. Eisner, A., T. Perlstein and W.C. Ault, JAOCS 40:594 (1963).
4. Ault, W.C., and A. Eisner, JAOCS 39:132 (1962).
5. Eisner, A., T. Perlstein and W.C. Ault, JAOCS 39:290 (1962).
6. Nakano, Y., and T.A. Foglia, JAOCS 61:569 (1984).
7. Barrett, F.O., and C.G. Goebel, U.S. Patent 3,074,983 (1963).
8. Sakauchi, N., and E.C. Horning, Anal. Lett. 4:41 (1971).
9. Benesi, H.A., J. Phys. Chem. 61:970 (1957).
10. Loev, B., and J.T. Massengale, J. Org. Chem. 22:988 (1957).
11. Smith, F.D., H.E. Kenney and A.J. Stirton, J. Org. Chem. 30:885 (1965).
12. Smith, F.D., A.J. Stirton and C.J. Dooley, JAOCS 45:747 (1968).
13. Smith, F.D., and A.J. Stirton, JAOCS 48:160 (1971).

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